

Imaging light-induced molecular fragmentation dynamics

by

Travis Severt

B.S., California Lutheran University, USA, 2012

AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the
requirements for the degree

DOCTOR OF PHILOSOPHY

Department of Physics
College of Arts and Sciences

KANSAS STATE UNIVERSITY
Manhattan, Kansas

2021

Abstract

When a molecule absorbs energy from its surrounding environment, the molecule’s structure begins to evolve. Understanding this evolution at a fundamental level can help researchers, for example, steer chemical reactions to more favorable outcomes. The research reported in this thesis aims to further knowledge about molecular fragmentation dynamics using coincidence three-dimensional momentum imaging. To achieve this goal, we use a combination of ultrafast, intense laser pulses and vacuum-ultraviolet single-photon absorption to initiate and probe molecular dynamics. Specifically, ultrafast lasers allow researchers to follow and control molecular dynamics on their natural time scales. To complement such studies, we also use vacuum-ultraviolet single-photon absorption, in conjunction with the coincidence momentum imaging of all ejected fragments including electrons, to pinpoint state-selective dynamics occurring in various molecular targets.

Throughout the thesis, we are interested in several different classes of molecular dynamics. First is the sequential fragmentation of molecules, where two or more bonds break in a step-wise manner. Specifically, we developed the native-frames analysis method, which is used to systematically reduce the dimensionality of multi-body fragmentation using the conjugate momenta of Jacobi coordinates. Applying this framework, we identify the signature of sequential fragmentation and separate its distribution from other competing processes. Moreover, we highlight the method’s strengths by following fragmentation dynamics step-by-step and state-selectively using the single-photon double-ionization of D_2O as an example. In addition, we explore how the signature of sequential fragmentation within the native-frames method may change under different initial conditions and demonstrate the first steps toward expanding the method to four-body breakup using formic acid as an example. In the future, we hope to identify exotic sequential fragmentation pathways where two or more metastable intermediates are formed together.

We also explore molecular isomerization and roaming dynamics leading to bond rearrangement. Specifically, we demonstrate that bond-rearrangement branching ratios in several triatomic molecules are approximately the same order of magnitude. Furthermore, we highlight that the formation of H_3^+ in various alcohol molecules can occur via roaming of H_2 molecules. In addition, we study the coherent control of several molecular ions, demonstrating that the CS^{2+} molecule fragments via a pump-dump mechanism that occurs in a single laser pulse. We also explore the two-color control of D_2^+ dissociation. Specifically, we observe phase shifts between pathways originating from different initial vibrational levels corresponding to “time-delays” of 10’s of attoseconds, showing that such time-scales are not just accessible via electron dynamics.

Since single vacuum-ultraviolet photon absorption experiments have proven to be powerful in studying molecular fragmentation dynamics, we investigate the enhancement of lab-based high-order harmonic generation photon sources driven by two-color laser fields. Specifically, we show that two-color 800–400-nm and 800–266-nm driving fields outperform the single-color 800-nm driver by more than an order of magnitude for the plateau harmonics. Furthermore, we demonstrate that the 800–266-nm bichromatic field can control the excursion time of an electron’s trajectory by as much as a factor of 2. This result is important for techniques that use the rescattering electron wavepacket as a probe for molecular dynamics, such as in laser-induced electron diffraction (LIED) and high-harmonic spectroscopy (HHS) techniques.

Finally, we highlight an upgrade of our coincidence three-dimensional momentum imaging method to measure breakup channels of molecular ions where the fragments have large mass-to-charge ratio differences. Specifically, we detect the light ions, such as H^+ and H_2^+ , by adding a second movable offset detector closer to the interaction region. Meanwhile, the heavy ions and neutral fragments fly underneath the new detector and are measured using the original downstream detector, as demonstrated with preliminary CD_2^+ measurements.

In closing, this thesis covers a variety of topics with the common theme of better understanding molecular fragmentation dynamics, ranging from multi-body fragmentation dynamics to isomerization, roaming, and coherent control. In addition, we discuss enhancing

high-harmonic-generation-based photon sources to help assist in such studies in the future. Overall, we believe the results presented throughout this thesis contribute to the advancement of molecular dynamics research.

Imaging light-induced molecular fragmentation dynamics

by

Travis Severt

B. S., California Lutheran University, USA, 2012

A DISSERTATION

submitted in partial fulfillment of the
requirements for the degree

DOCTOR OF PHILOSOPHY

Department of Physics
College of Arts and Sciences

KANSAS STATE UNIVERSITY
Manhattan, Kansas

2021

Approved by:

Major Professor
Itzik Ben-Itzhak

Copyright

© Travis Severt 2021.

Abstract

When a molecule absorbs energy from its surrounding environment, the molecule’s structure begins to evolve. Understanding this evolution at a fundamental level can help researchers, for example, steer chemical reactions to more favorable outcomes. The research reported in this thesis aims to further knowledge about molecular fragmentation dynamics using coincidence three-dimensional momentum imaging. To achieve this goal, we use a combination of ultrafast, intense laser pulses and vacuum-ultraviolet single-photon absorption to initiate and probe molecular dynamics. Specifically, ultrafast lasers allow researchers to follow and control molecular dynamics on their natural time scales. To complement such studies, we also use vacuum-ultraviolet single-photon absorption, in conjunction with the coincidence momentum imaging of all ejected fragments including electrons, to pinpoint state-selective dynamics occurring in various molecular targets.

Throughout the thesis, we are interested in several different classes of molecular dynamics. First is the sequential fragmentation of molecules, where two or more bonds break in a step-wise manner. Specifically, we developed the native-frames analysis method, which is used to systematically reduce the dimensionality of multi-body fragmentation using the conjugate momenta of Jacobi coordinates. Applying this framework, we identify the signature of sequential fragmentation and separate its distribution from other competing processes. Moreover, we highlight the method’s strengths by following fragmentation dynamics step-by-step and state-selectively using the single-photon double-ionization of D_2O as an example. In addition, we explore how the signature of sequential fragmentation within the native-frames method may change under different initial conditions and demonstrate the first steps toward expanding the method to four-body breakup using formic acid as an example. In the future, we hope to identify exotic sequential fragmentation pathways where two or more metastable intermediates are formed together.

We also explore molecular isomerization and roaming dynamics leading to bond rearrangement. Specifically, we demonstrate that bond-rearrangement branching ratios in several triatomic molecules are approximately the same order of magnitude. Furthermore, we highlight that the formation of H_3^+ in various alcohol molecules can occur via roaming of H_2 molecules. In addition, we study the coherent control of several molecular ions, demonstrating that the CS^{2+} molecule fragments via a pump-dump mechanism that occurs in a single laser pulse. We also explore the two-color control of D_2^+ dissociation. Specifically, we observe phase shifts between pathways originating from different initial vibrational levels corresponding to “time-delays” of 10’s of attoseconds, showing that such time-scales are not just accessible via electron dynamics.

Since single vacuum-ultraviolet photon absorption experiments have proven to be powerful in studying molecular fragmentation dynamics, we investigate the enhancement of lab-based high-order harmonic generation photon sources driven by two-color laser fields. Specifically, we show that two-color 800–400-nm and 800–266-nm driving fields outperform the single-color 800-nm driver by more than an order of magnitude for the plateau harmonics. Furthermore, we demonstrate that the 800–266-nm bichromatic field can control the excursion time of an electron’s trajectory by as much as a factor of 2. This result is important for techniques that use the rescattering electron wavepacket as a probe for molecular dynamics, such as in laser-induced electron diffraction (LIED) and high-harmonic spectroscopy (HHS) techniques.

Finally, we highlight an upgrade of our coincidence three-dimensional momentum imaging method to measure breakup channels of molecular ions where the fragments have large mass-to-charge ratio differences. Specifically, we detect the light ions, such as H^+ and H_2^+ , by adding a second movable offset detector closer to the interaction region. Meanwhile, the heavy ions and neutral fragments fly underneath the new detector and are measured using the original downstream detector, as demonstrated with preliminary CD_2^+ measurements.

In closing, this thesis covers a variety of topics with the common theme of better understanding molecular fragmentation dynamics, ranging from multi-body fragmentation dynamics to isomerization, roaming, and coherent control. In addition, we discuss enhancing

high-harmonic-generation-based photon sources to help assist in such studies in the future. Overall, we believe the results presented throughout this thesis contribute to the advancement of molecular dynamics research.

Table of Contents

List of Figures	xiii
List of Tables	xv
Acknowledgements	xvi
Dedication	xviii
Preface	xix
1 Introduction and Motivation	1
1.1 Ultrafast and strong-field physics	2
1.2 Our interests	4
1.3 Document Organization	6
2 Experimental methods: coincidence momentum imaging	7
2.1 General Background	7
2.2 Light sources	9
2.2.1 Ultrafast Laser	10
2.2.2 Synchrotron	11
2.3 Coincidence momentum imaging using COLTRIMS	11
2.3.1 Imaging molecular fragmentation	12
2.3.2 Determining momentum of an unmeasured fragment	15
2.3.3 Imaging electrons	16
2.4 Coincidence momentum imaging of ‘fast’ molecular-ion beams	17

2.5	Imaging mass asymmetric fragmentation channels	18
3	Imaging multi-body sequential fragmentation: native frames analysis	22
3.1	Background and motivation	22
3.2	Disentangling sequential from concerted fragmentation	26
3.3	Imaging sequential fragmentation step-by-step and state-selectively	34
3.4	Native frames method tutorial	45
3.5	Sequential fragmentation in the non-planar NH_3 molecule	71
3.6	Towards four-body sequential fragmentation	88
3.6.1	Four-body Jacobi coordinates and their conjugate momenta	88
3.6.2	Four-body fragmentation of HCOOD	91
3.7	Summary and outlook	93
4	Bond rearrangement in polyatomic molecules	95
4.1	Introduction	95
4.2	Bond rearrangement in triatomic molecules	98
4.3	H_2 roaming in alcohol molecules	110
4.4	Summary and outlook	122
5	Coherent control of molecular ions	123
5.1	Introduction	123
5.2	Pump-dump control mechanism in CS^{2+}	125
5.3	Two-color control of the dissociation of D_2^+	133
5.4	Summary and outlook	137
6	Enhancing high-order harmonic generation driven by two-color laser fields	139
6.1	Introduction	139
6.1.1	What is high-order harmonic generation?	140
6.1.2	Three-step model and classical electron trajectories	141

6.1.3	Odd and even harmonics	143
6.1.4	Short and long electron trajectories	144
6.1.5	Micro- and macro-scopic efficiency mechanisms	145
6.1.6	Enhancing HHG's photon flux	147
6.1.7	Classical electron trajectories in $\omega - n\omega$ fields	148
6.2	Experimental methods	149
6.3	Enhancing high-order harmonic generation by controlling the diffusion of the electron wavepacket	150
6.4	Enhancing HHG in $\omega - 2\omega$ and $\omega - 3\omega$ fields	165
6.5	Summary and outlook	177
7	Summary and Outlook	178
	Bibliography	182
A	Three-dimensional momentum imaging	202
A.1	COLTRIMS Imaging	202
A.1.1	TOF proportional to $\sqrt{m/q}$	202
A.1.2	Imaging equations along Z axis	204
A.1.3	Identifying and selecting coincidence channels	205
A.2	Imaging molecular-ion beams	207
A.2.1	The Z-Dimension (TOF axis)	207
A.2.2	The X-Dimension (Deflector axis)	210
B	Supplementary material for H ₂ roaming manuscript	212

List of Figures

2.1	Typical laser intensity profiles	10
2.2	Schematic of COLTRIMS	13
2.3	Schematic of ion beam imaging method	17
2.4	Schematic of upgraded ion beam imaging method	18
2.5	CD_2^+ two-detector example	19
2.6	Two-detector coincidence TOF	20
3.1	Newton diagram and Dalitz plot example	24
3.2	Single-photon vs multiphoton absorption	35
3.3	Sequential fragmentation of NH_3	72
3.4	Formic acid ball-and-stick model	88
3.5	Four-body Jacobi coordinates	89
3.6	Four-body breakup of HCOOD	93
4.1	Schematic of transition states	96
5.1	Schematic of pump-dump and two-color control	124
5.2	Collinear two-color setup	133
5.3	D_2^+ two-color KER and fragmentation pathways	134
5.4	D_2^+ two-color $N(\text{KER}, \cos\theta)$ distributions	135
5.5	D_2^+ two-color phase dependence for different initial vibrational states	136
6.1	Schematic of typical setup for HHG	140
6.2	Schematic of three-step model for HHG	141
6.3	Electron trajectories in single-color field	142

6.4	Long and short electron trajectories	144
A.1	Calibrating TOF direction in COLTRIMS	204
A.2	Example CTOF spectra of ethanol	205
A.3	Two-body momentum gate for identifying fragmentation channels	207

List of Tables

5.1	The relative phase shifts between pairs of vibrational states, $\Delta\phi_{v,v'}$, and the associated time-delays, $\Delta\tau_{v,v'}$	137
-----	--	-----

Acknowledgments

I am forever thankful to the many people who helped me progress throughout my journey to earning my PhD. There are far too many people to list, but everyone I interacted with throughout my adventures were instrumental. I am thankful to all of you.

First off, I would like to thank my advisor Itzik Ben-Itzhak, who taught me how to be passionate, thorough, skeptical, and optimistic about our work. I also would like to thank him for being patient while I struggled through and learned the necessary skills to succeed in the lab. I would also like to thank Kevin Carnes for helping me improve my writing and grammar, and with writing and modifying SpecTcl, which was vitally important to collect the data in our experiments.

I also want to thank the research groups of Brett Esry, Artem Rudenko, Daniel Rolles, Carlos Trallero, Eric Wells, Thorsten Weber, Daniel Slaughter, Reinhard Dörner, Alan Landers, Joshua Williams, and Marcos Dantus, who all collaborated with us over many years and helped me learn about many different experimental techniques and physical processes that I would not have been exposed to otherwise. I also would like to thank all of the JRML support staff for their help designing, building, and troubleshooting our experimental setups. I would also like to thank Charles Fehrenbach for extensive help with the ECR ion source and PULSAR laser. In addition, it is important to thank Kristan Corwin and Larry Weaver for giving me the opportunity to come to K-State as an REU student. Without that experience, it is unlikely that I would have made it to where I am today.

I also want to thank my family for making sacrifices and helping throughout the ups and downs along the way. Without all of your love and support, I would never have made it to where I am today. Thank you!

Finally, I want to thank the funding agencies that supported my research. Specifically, the high-order harmonic generation work presented in Section 6 and I (while performing that work) were partially supported by the National Science Foundation under Award No. IIA-

1430493. For the rest of my work, I, the JRML personnel, and operations were supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office for Science, U.S. Department of Energy under Award # DE-FG02-86ER13491.

Dedication

Dedicated to my family.

Preface

In this dissertation, we focus on two different research avenues. The majority of the thesis concentrates on studies of molecular fragmentation dynamics using coincident three-dimensional momentum imaging. The remainder of the thesis explores enhancing high-order harmonic generation (HHG) employing two-color driving laser-fields. Since the background needed to understand these subjects, the experimental methods, and results are different, we present these topics separately. Specifically, Chapters 2 through 5 focus on molecular dynamics while Chapter 6 contains our HHG research.

Chapter 1

Introduction and Motivation

Throughout my Ph.D. research, we have used ultrafast and intense laser pulses [1–3] to study molecular fragmentation dynamics. Due to the laser pulse’s high intensity, the molecules may absorb and emit many photons, leading to their (multiple) ionization and subsequent dissociation [4–6]. Our goal is to elucidate the molecular fragmentation dynamics by imaging the three-dimensional momentum distributions of the resulting fragments long after their interaction with the laser [7–11], i.e. asymptotically. With such information, we hope to gain insight into the molecule’s fragmentation pathways and how the intense laser pulses manipulate them.

In some cases, the intense ultrafast laser fields complicate the dynamics’ interpretation because of their broad bandwidth and the difficulty to determine the net number of photons absorbed. Therefore, to supplement these measurements, we also study the fragmentation dynamics initiated by a single vacuum ultraviolet photon produced by a synchrotron light source. In this case, by measuring the momenta of all charged fragments emitted during the interaction, we can pinpoint the states where the dynamics begin and end, allowing us to identify the fragmentation pathways [12, 13].

In this chapter, we introduce the field of ultrafast and strong-field physics. The goal is to frame how our research fits into the field and how our approaches can help advance it.

1.1 Ultrafast and strong-field physics

Ultrafast and intense laser pulses allow researchers to study and manipulate light-matter interactions through a variety of means. First, the “strong” electric fields produced by the “intense” laser can manipulate matter in new ways previously unavailable in the “weak”-field regime. Specifically, the laser pulses’ peak intensity is large enough (typically greater than 10^{11} W/cm²) so that the probability of multi-photon absorption and/or stimulated emission is high [14–16]. One popular example is the low energy above threshold ionization (ATI) peaks [17], which occur when more photons are absorbed than necessary to ionize the atom or molecule. Furthermore, by the absorption and emission of photons, researchers can also access states of the system that are dipole forbidden in single-photon transitions, potentially preparing exotic states of matter not usually accessible [18, 19].

Furthermore, the laser pulse’s electric field can become comparable to the binding fields of the valence electrons in an atom, molecule, or material (like nanoparticles or surfaces), enabling the manipulation of the electrons and their ionization [1, 2, 14]. In the first case, the intense fields can AC Stark shift states into resonance, enhancing multiphoton transitions to them [14, 20]. Alternatively, after an electron is ionized, the field is strong enough to modify the resulting continuum electron wavepacket, accelerating part of it back towards the remaining target where several processes fundamental to strong-field physics can occur. Specifically, the returning parts of the wavepacket can recombine with the remaining target and emit vacuum ultraviolet to soft X-ray photons in a process known as high-order harmonic generation (HHG) [1, 2, 14]. Alternatively, the electron may elastically rescatter off the remaining ion, resulting in the high energy ATI peaks [2, 14], or inelastically rescatter off the target and further ionize it in a process known as nonsequential double ionization (NSDI) [1, 2, 14, 17, 21]. In the case of molecules, the intense fields can mix electronic states, which may be represented using “field-dressed” states [6]. Specifically, the intense fields lead to avoided crossings between the “dressed” states, leading to phenomena like bond softening [6, 22]. These examples show that these strong laser-fields have enabled the discovery of many new, interesting, and potentially useful phenomena.

The second useful characteristic of the intense laser pulses is their ultrashort duration, typically defined as picoseconds or shorter [23]. With these intense and ultrafast pulses, researchers can place the target in non-equilibrium conditions and then time-resolve the resulting dynamics. The idea is that the laser can be used as a camera shutter, allowing one to take “snapshots” of the dynamics as a function of time [24–27], thus making a “molecular movie” of the dynamics. The laser’s specific pulse duration used in such studies depends on the dynamics of interest and typically needs to be much shorter than the timescales of the dynamics. Specifically, rotational dynamics usually occur on picosecond timescales, while nuclear/vibrational dynamics take place on time scales of 10’s of femtoseconds, and electron dynamics take place on the 10’s to 100’s of attoseconds [2]. Studies focusing on these different timescales have led to the creation of several research fields, such as femtochemistry [24, 28] and attophysics [2, 29–31].

An important consequence of the ultrashort pulse durations is the large spectral bandwidth of the pulses, which lead to the excitation of a broad coherent superposition of states that may evolve towards indistinguishable final states. Then, by tuning the laser’s electric field, one can modify the interference of the superposed states to drive the system towards more favorable outcomes, which is known as coherent control [32–34]. One may accomplish this by changing the intensity, bandwidth, dispersion, and carrier-envelope-phase of the laser pulse or by adding additional fields such as in pump-dump, or two-color control [34].

Throughout this dissertation, we use a combination of the above characteristics of ultrafast and intense lasers to study and influence molecular fragmentation dynamics. Generally, it is challenging to disentangle the ways strong laser fields influence molecular dynamics [35–38]. Therefore, we try to use experimental approaches to simplify the interpretation, as we discuss in the next section. In some cases, we go a step further and supplement our experiments using single-photon (about 60 eV) absorption, which simplifies tracking the dynamics that occur.

1.2 Our interests

Our research group’s main interest is to experimentally investigate molecular dynamics initiated by intense ultrafast laser pulses. In this document, we continue along this theme, using the experimental approaches “best” suited for the physics we are interested in studying.

Historically, our group implements a coincidence three-dimensional momentum imaging technique to study the dissociation of fast molecular ion beams following their interaction with an intense laser pulse [11, 39, 40]. By using a molecular ion-beam target traveling with a few keV, our method enables the detection of neutral and ionic fragments since they all impact the detector with sufficient kinetic energy to activate it. Our approach may simplify the interpretation of molecular dynamics since we do not need to ionize the molecule or its fragments to detect them, in contrast to what other momentum imaging methods commonly require. Furthermore, since molecular ions typically only need to absorb a few photons to dissociate [6, 11], the experiments can be conducted at much lower intensities, reducing the number of potential fragmentation pathways. In the past, we have successfully implemented this method on benchmark systems like the one-electron H_2^+ [11, 41–45] and the simplest triatomic molecule H_3^+ [46–49]. Such measurements allow for more straightforward comparisons with theory in contrast to more complex diatomic and triatomic molecules where further approximations must be invoked to describe the dynamics theoretically. Despite their further complications, we have extended our imaging method to more complex multi-electron diatomic [50–54] and polyatomic molecules [55, 56]. In this thesis, we continue such measurements, studying the fragmentation dynamics of a CS^{2+} ion beam (Section 5.2) and controlling the dissociation dynamics of a D_2^+ ion beam in two-color laser fields (Section 5.4).

To extend our studies along this path to more complex polyatomic molecular ion beams, we have upgraded our imaging method to measure light and heavy ionic fragments simultaneously. Previously, our imaging of mass asymmetric molecules, like CD_2^+ , was limited by the large deflection of light D^+ fragments and small deflection of the heavy CD^+ fragments relative to the deflection of the target beam [54]. To overcome this issue, we have upgraded the system by adding a second detector that can measure the light fragments, as we explain

in Section 2.5.

Another interest pursued in this thesis is the multi-body fragmentation dynamics induced by strong-laser fields. While ion-beam measurements can help simplify the interpretation of molecular dynamics, their main drawback is the low target density, which typically corresponds to low acquisition rates. When molecules breakup into three or more fragments, we record higher dimensional data and need more counts to view it differentially with sufficiently small error bars. To this end, we change approaches and use intense lasers to multiply ionize and fragment neutral polyatomic molecules, which have orders of magnitude higher target density than their ion beam counterparts and thus increases acquisition rates. In addition, the advantage of beginning with neutral molecules is that their initial conditions are well known since they are typically cold¹, in contrast to molecular ion beams which may be in excited electronic, vibrational, and rotational states.

While our interests in strong-field induced multibody molecular fragmentation are more general, this document focuses on sequential breakup (Chapter 3), that is breakup where two or more bonds break in a stepwise manner [57–59]. Specifically, we developed the native-frames method that facilitates the systematic reduction of the data’s dimensionality by using Jacobi coordinates’ conjugate momenta. We then extend this analysis to identify the signature of sequential fragmentation and separate it from other competing processes using the coincidence three-dimensional momentum distributions [60].

Furthermore, even though strong laser fields are a useful and convenient tool for us to use, we performed a few sequential fragmentation studies following the absorption of a single (approximately 60 eV photon) produced by a synchrotron (Sections 3.3 and 3.5). This approach’s advantage is that we can better determine where the dynamics start, i.e. the electronic states initially populated, because there is less uncertainty in the amount of energy that is deposited into the system compared to a strong-laser field. Therefore, these measurements can complement studies using strong-laser fields. Specifically, in the single-photon sequential fragmentation studies, we show that we can identify the competing

¹Typically, small molecules are in the lowest electronic and vibrational states. On the other hand, the rotational temperatures tend to be on the order of 50-100 K.

electronic states contributing to the sequential breakup during each breakup step.

We also study more exotic bond-rearrangement fragmentation processes induced by strong-laser fields. In this case, we also ionize neutral molecules because the bond rearrangement channels typically have low production rates [61]. Specifically, we study bond rearrangement in several triatomic molecules (Section 4.2). In other words, for a linear or slightly bent ABC triatomic molecule, we study the production of an $AC^+ + B^+$ fragmentation channel. We also study the formation of H_3^+ from a variety of alcohol molecules (Section 4.3).

Finally, we explore the production of a higher-flux vacuum-ultraviolet photon source based on HHG for studying molecular dynamics (Chapter 6). Specifically, we show that by driving HHG with two-color $\omega - 3\omega$ laser fields, we can enhance the harmonics photon flux by at least one order of magnitude over the single-color driving field. In the future, we hope to implement such a source in our molecular fragmentation studies.

1.3 Document Organization

The following describes the structure of the thesis, which mainly focuses on our investigations of molecular dynamics. The following chapter describes the experimental methods used to study the molecular fragmentation dynamics, which includes descriptions of the light sources and the coincidence momentum imaging techniques we employ. Chapter 3 presents our studies of sequential fragmentation following three- and four-body fragmentation of polyatomic molecules. Chapter 4 explores bond rearrangement in a several molecules, including “simple” triatomic molecules and more complex alcohols. Meanwhile, chapter 5 contains a couple of studies on the coherent control of the fragmentation dynamics of molecular ions using conventional control schemes, like pump-dump and two-color control. Chapter 6 is a self-contained description of our work on creating a brighter vacuum-ultraviolet photon source using high-order harmonic generation. Finally, a summary and possible future directions are presented in Chapter 7.

Chapter 2

Experimental methods: coincidence momentum imaging

In this chapter, we present the experimental methods used to study photo-induced molecular fragmentation dynamics. Specifically, we describe the light sources used to initiate the fragmentation dynamics as well as the coincidence three-dimensional momentum imaging techniques we employ to gain insight into the breakup of molecules.

2.1 General Background

To study molecular dynamics, researchers use a variety of techniques that generally fall into two categories. The first category involves techniques which destroy the molecule, using charged particle impact or photon absorption, and measure the molecular fragments. Some popular techniques that fall into this category are mass spectrometry [62–65], photoelectron spectroscopy [66–71], velocity map imaging (VMI) [72–75], covariance mapping [76–78], and coincidence three-dimensional momentum imaging (like COLTRIMS) [7–11, 37].

The second category involves techniques that do not necessarily require the destruction of the molecule since they do not measure fragments. Some examples include photoabsorption [79–81] and nuclear magnetic resonance (NMR) spectroscopy [82, 83], as well as

electron [84–89] and X-ray diffraction [90–93]. In the latter cases, the molecule is likely destroyed, however, information about the configuration of the molecule is extracted (hopefully before destruction) from the diffraction patterns and not the fragments themselves. Recently, electron and X-ray diffraction techniques have been improved, allowing for time resolved measurements since the development of new ultrafast electron sources [85–87] and high intensity X-ray pulses from free-electron lasers [94–96].

It is important to note that these methods are complimentary, each with its own strengths and weaknesses. For example, absorption- and diffraction-based methods can directly focus on dynamics occurring in the neutral molecule [85–87, 92, 93]. On the other hand, when methods that image ions and photoelectrons are used to study dynamics in the neutral [97], their observables are convolved with dynamics that also involve cationic states. Therefore, no one method can give a complete picture, and researchers use various techniques to understand molecular dynamics.

Our group primarily studies molecular breakup, i.e. the destruction of the molecule, that is initiated by either an intense laser pulse [98] or the absorption of a vacuum ultraviolet photon provided by a synchrotron light source [99, 100]. We measure the resulting fragments using coincidence three-dimensional momentum imaging techniques that can determine the momentum of each fragment ejected during the breakup and associate them all with the same molecule [7–11, 37]. This measurement allows us to look at the kinetic energy release distributions, momentum correlations between fragments, and angular distributions to help understand the breakup dynamics. The main disadvantage of this method compared to other destructive techniques is the low detection rates, which need to be kept below one molecule’s fragmentation per laser shot. If multiple molecules break during a single laser shot, it becomes difficult to properly correlate the fragments coming from the same molecule.

In this thesis, we use two momentum imaging techniques, each with its own merits. The primary technique we employ is known as cold-target recoil ion momentum spectrometry (COLTRIMS) [7–10], which is briefly described in Section 2.3. Using this method, we can measure all ions and electrons ejected from the same molecule, making the measurement kinematically complete if there are no neutral fragments. Then, the measured momentum

distributions can be used to identify fragmentation pathways and mechanisms. The drawback of this method is that neutral fragments cannot be measured, though their momenta can be evaluated in some instances, as we describe in Section 2.3.2.

Secondly, we utilize a coincidence momentum imaging method to study the fragmentation of “fast” (a few keV) molecular ion beams [11, 41], which we explain further in Section 2.4. Since the molecular-ion beam already travels with a few keV toward the detector, any neutral fragment can be detected since it has large enough impact energy to activate the detector. The drawback of this method is that the ion-beam target has very low density, usually a few orders of magnitude below the density of the background gas in our ultrahigh vacuum chamber. Such low density typically corresponds to low data acquisition rates. Fortunately, since we perform coincidence measurements, can tune the experimental conditions to avoid the dominant background contaminants, and can take advantage of the fact that cations usually have large dissociation probabilities, such experiments are feasible.

Finally, we describe progress in upgrading our coincidence molecular ion beam imaging method to measure mass asymmetric breakup channels. Specifically, we have improved the setup by adding a second movable detector to measure the light ionic fragments. This upgrade enables, for example, studying hydrogen elimination versus deprotonation from hydrocarbons.

2.2 Light sources

The experiments throughout this thesis use two different light sources to initiate molecular fragmentation dynamics. Specifically, we use an ultrafast laser [98] to initiate the dynamics via multiphoton absorption and then to control them. Alternatively, we use a synchrotron light source [99, 100] to initiate the molecular fragmentation dynamics via single-photon absorption.

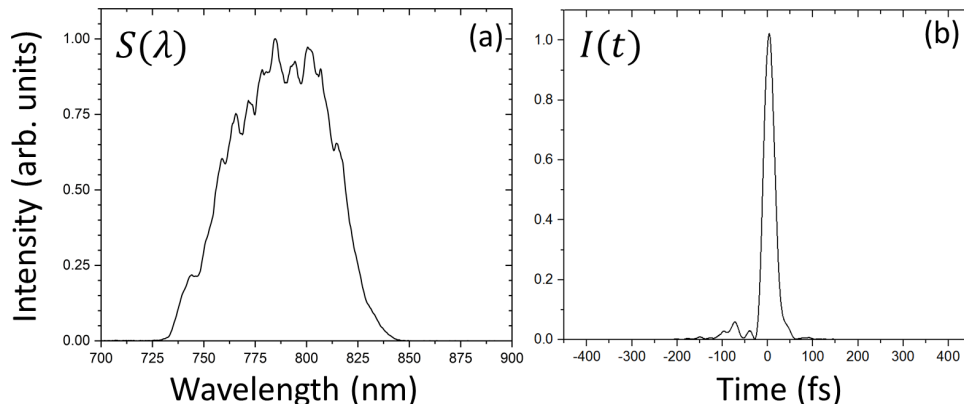


Figure 2.1: Typical (a) measured spectral and (b) temporal intensity profiles for the PULSAR laser. In this measurement, the pulse duration was approximately 29 fs.

2.2.1 Ultrafast Laser

The majority of the experiments presented in this document use an ultrafast laser to ionize and/or fragment molecules. Specifically, we use a Ti:Sapphire laser in the James R. MacDonald Laboratory, called PULSAR, which produces linearly polarized pulses with a central wavelength typically centered around 780 nm. The pulse duration is usually 22-30 fs, with pulse energies up to 2 mJ at a repetition rate of 10 kHz.

To measure the laser’s pulse duration, we use the frequency-resolved-optical-gating (FROG) technique [101]. From these measurements, we can determine the laser pulse’s spectral intensity and phase, thus allowing us to evaluate temporal structure of the pulse using a Fourier transform. In Fig. 2.1, we show a typical measured spectrum, i.e. the spectral intensity, and temporal envelope of the PULSAR laser in our experiments.

Finally, the ultrafast laser is focused onto a molecular target, where the peak intensities can reach up to approximately 10^{15} W/cm² for the data presented in this document. It is important to note that due to the spatial profile of a focusing Gaussian beam, not all molecules are exposed to the laser’s peak intensity because they are not located directly in the focus, but shifted slightly off-axis. Generally, most molecules interacting with the laser are exposed to lower intensities because of the larger interaction volume between the laser and molecular target. This effect is known as focal volume averaging and generally needs to be considered when comparing experiments to theory.

2.2.2 Synchrotron

A couple of the experiments presented in this thesis were performed at the Advanced Light Source (ALS) synchrotron located at the Lawrence Berkeley National Laboratory (LBNL). Briefly, synchrotrons are accelerator-based light sources that use the bremsstrahlung emitted from relativistic electron beams to produce microwave to hard X-ray radiation [99, 100]. Then, a monochromator selects the photon energy and bandwidth of interest, where the bandwidth is typically tens of meV. Such energy tunability and narrow bandwidth allows for state specific excitation. The pulse duration is on the order of 100 ps at a repetition rate of a few MHz. Since the intensity of synchrotron light sources are low, all of our studies are in the linear regime, in contrast to ultrafast lasers where the interactions are nonlinear. Therefore, focal volume averaging does not generally need to be considered in these experiments.

We conduct our experiments at ALS beamline 10.0.1.3, which we tune to provide approximately 61 eV photons with a bandwidth smaller than ± 50 meV. We choose this photon energy because it doubly ionizes the molecules under study, like D_2O and NH_3 , and allows access to several excited dicationic states of interest.

2.3 Coincidence momentum imaging using COLTRIMS

A COLTRIMS apparatus, shown schematically in Fig. 2.2, allows us to measure both the ions and electrons emitted from the ionization of a single atom or molecule [7–10]. Briefly, the target gas is introduced into the vacuum chamber via adiabatic expansion through a small (typically on the order of 50 μm diameter) nozzle and is collimated using a series of skimmers and slits. Throughout the expansion, molecules rotationally and, to a smaller extent, vibrationally cool due to collisions during the initial expansion [102, 103], which convert the internal energy into translational motion. In the end, this results in a cold supersonic beam entering the vacuum chamber, where it intersects a focused photon beam. The temperature of the supersonic beam depends on the driving pressure of the gas jet (typically a few atmospheres) and if a He buffer gas is included to further cool the jet. Typically, the

molecule’s electronic and vibrational temperatures are around room temperature, while the rotational temperature is around 50-100 K. In addition, the jet’s temperature transverse and parallel to its propagation direction are about 5 and 100 K, respectively¹.

After the molecule interacts with the focused light, which is typically polarized along the Z axis, the resulting positive ions are accelerated toward a time- and position-sensitive detector by a uniform electric field. On the other hand, the electrons are accelerated in the opposite direction toward a second time- and position-sensitive detector. To confine the electrons within the diameter of that detector, a magnetic field is introduced parallel to the electric field, i.e. along the time-of-flight (TOF) axis, making the electrons undergo cyclotron motion. Note that in some COLTRIMS experiments, we only measure the resulting ions for simplicity.

From the time and position information of the hits on the detector, we calculate the three-dimensional momentum of each detected charged fragment emitted from a single atom or molecule. Then, we associate all the fragments originating from the same molecule and calculate the center-of-mass momenta of the recoiling molecular ion using momentum conservation. In the next few sections, we describe how we compute the momenta of ions, electrons, and even unmeasured neutral fragments on an event-by-event basis from the measured positions and TOFs.

2.3.1 Imaging molecular fragmentation

To describe how we calculate the momenta from the measured positions and TOFs, we consider the N-body fragmentation of an arbitrary molecule for which all fragments are measured in coincidence. The idea is to calculate the momentum of each fragment in the recoiling center-of-mass frame of the resulting molecular ion. To do this, we measure the positions x_j and y_j as well as the time-of-flight T_j , where the j subscript represents the j th fragment. The following discussion is limited to the field free directions (i.e. the X and Y

¹Note that the jet’s temperature can be estimated by the molecule’s center-of-mass momenta obtained from the COLTRIMS analysis described below. To extract the temperature information, we assume that the ejected electron’s contributions to the distribution of the center-of-mass momenta is negligible

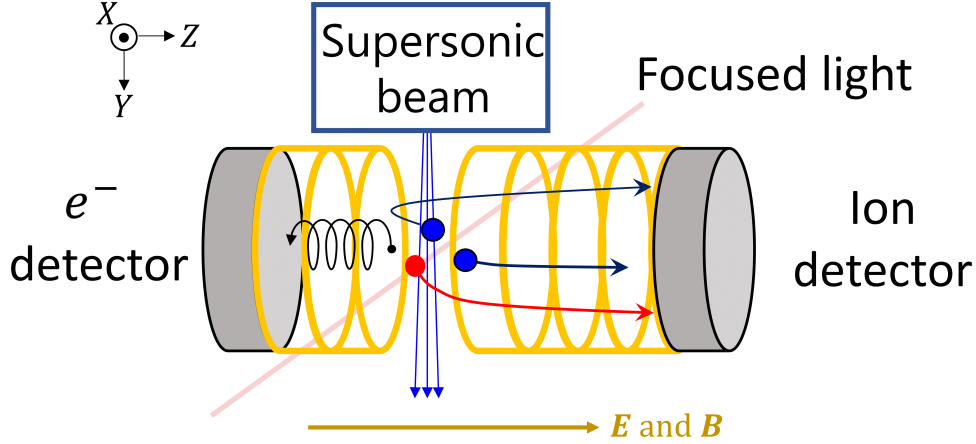


Figure 2.2: Schematic of a COLTRIMS setup (see text for explanation). The laser and synchrotron polarization is typically aligned along the Z axis.

dimensions in Fig. 2.2) for simplicity. For the derivations of the expressions along the TOF (Z) axis, see Appendix A.1.1.

First, it is important to note that T_j is not the time between laser interaction with the molecule and the detection of the fragment, which we call the true TOF. There is typically a small offset t_0 due mainly to the detector response and its corresponding electronics (we describe how to find t_0 in Appendix A.1.1). Therefore, we must first calculate the true time-of-flight t_j as

$$t_j = T_j - t_0. \quad (2.1)$$

To determine the final X -momentum of each fragment in the center-of-mass, we solve a set of coupled kinematic equations given by:

$$x_j - x_0 = (v_{0x} + v'_{jx}) t_j, \quad (2.2)$$

for $j = 1, \dots, N$. Specifically, x_j and t_j are the measured positions and true TOFs of the j th fragment, respectively, v_{0x} is the center-of-mass velocity of the recoiling molecular ion after electron ejection, x_0 is the initial position where the fragmentation occurred with respect to the center of the detector, and v'_{jx} are the velocities of the fragments in the center-of-mass

frame mentioned above. In addition, we use the momentum conservation equation given by:

$$0 = \sum_{j=1}^N m_j v'_{jx}, \quad (2.3)$$

where m_j is the mass of the j th fragment. In total, we have $N + 1$ equations but $N + 2$ unknowns (v_{0x} , x_0 , and v'_{jx} for $j = 1, \dots, N$). Therefore, we have to choose one unknown, v_{0x} or x_0 , and keep it constant for all of the events, which we refer to as the average value of the distribution. Then, we solve for the remaining unknowns. The average value is estimated by taking advantage of the expected symmetries due to the laser-molecule interaction, such as reflection symmetry in the forward/backwards direction of the linearly polarized “single” color fields or ϕ symmetry about the polarization. Then, the solution for v'_{jx} is

$$v'_{jx} = \frac{x_j - x_0}{t_j} - v_{0x}. \quad (2.4)$$

Substituting v'_{jx} into Eq. 2.3, we can solve for either v_{0x} or x_0 . Specifically, when letting $x_0 = \bar{x}_0$ the solution for v_{0x} for each individual event is

$$v_{0x} = \frac{1}{M} \sum_{j=1}^N m_j \left(\frac{x_j - \bar{x}_0}{t_j} \right), \quad (2.5)$$

where M is the total mass of the molecule and $\bar{x}_0$ is the average value of x_0 . Alternatively, by setting $v_{0x} = \bar{v}_{0x}$ the solution of x_0 for each event is

$$x_0 = \left(\sum_{j=1}^N \frac{m_j x_j}{t_j} - M \bar{v}_{0x} \right) \left(\sum_{j=1}^N \frac{m_j}{t_j} \right)^{-1}. \quad (2.6)$$

The choice between setting x_0 or v_{0x} to be a constant depends on the experimental conditions and how each choice impacts the momentum resolution. For example, along the Y axis of our COLTRIMS, i.e. the axis parallel to the jet’s propagation direction, we expect a large spread in v_{0y} (typically has a temperature of 100 K) and a small spread in y_0 which is mostly due to the waist of the laser focus (typically 10’s of μm). Therefore, we choose

an average value of y_0 for all events and solve for v_{0y} for each molecule. In the remaining dimensions, the difference in the spread of v_{0x} and x_0 (or v_{0z} and z_0) is small enough such that choosing one variable or the other is equivalent. Therefore, we choose to solve for the $\mathbf{v}_0$ term in all dimensions for consistency.

Finally, the momentum of the j th fragment in the center-of-mass of the recoiling molecular ion is simply given by:

$$P_{jx} = m_j v'_{jx}. \quad (2.7)$$

Before continuing, it is important to note that the Y dimension is solved in the same manner. On the other hand, the coupled kinematic equations describing the fragment's motion along the TOF (Z) axis are more complex since they include the acceleration due to the electric field. We describe how to solve the equations along the TOF axis in Appendix A.1.1.

2.3.2 Determining momentum of an unmeasured fragment

In some cases, we can determine the momentum of an unmeasured fragment [12]. For example, the fragment may be unmeasured because it is neutral. Assuming we measure $N - 1$ fragments following N -body breakup, the imaging Eqs. 2.2 and 2.3 still apply. The difference is that we now have N equations (the $N - 1$ kinematic equations and conservation of momentum) and $N + 2$ unknowns. Therefore, to solve for the fragment velocities v'_{jx} , and hence momenta P_{jx} for all fragments in the center-of-mass frame of the recoiling molecular ion, we need to replace both x_0 and v_{0x} with their average values. In this case, we determine these values from other fragmentation channels for which we measure all the fragments in coincidence. Then, we can solve for P_{jx} , including for the unmeasured fragment.

There are two points to highlight from this brief discussion. First, if the missing fragment is a molecule, this method most likely cannot discern whether it is intact or fragmented. In such cases, the computed P_{jx} is the momenta of the center-of-mass of the unmeasured fragment. Secondly, the resolution of the P_{jx} distributions is worse than when we measure all the fragments in coincidence because we cannot correct event-by-event for the spread in the initial center-of-mass velocity. Fortunately, for COLTRIMS measurements, this is not a

significant problem because the laser focus is typically tight and the jet is usually cold and well collimated, meaning that the spread in initial positions and center-of-mass velocities is too small to significantly blur the resulting momentum images.

2.3.3 Imaging electrons

In the experiments conducted at the ALS in LBNL, we measured the electrons in coincidence with the emitted ions following the double ionization of each target molecule. Furthermore, calculating the electron momenta from the measured positions and time was the task of another member of the team. For this reason and since the analysis methods used for electron imaging in COLTRIMS are well documented in literature [9, 10], we limit the discussion to the important aspects of this imaging.

With only an electric field accelerating the electrons toward the “electron detector”, 4π collection efficiency is limited to very slow electrons because the faster electrons can easily fly off the detector. Therefore, to confine them within the radius of the detector, one employs a magnetic field parallel to the electric field, i.e. the TOF (Z) axis. The resulting force applied on the electron in the combined electric and magnetic fields, i.e. the Lorentz force, is

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v}_e \times \mathbf{B}) = q(v_{e,y}B\hat{\mathbf{x}} - v_{e,x}B\hat{\mathbf{y}} + E\hat{\mathbf{z}}). \quad (2.8)$$

Note that only the electric field $\mathbf{E}$ affects the electron motion along the Z axis. Therefore, the kinematic equation governing the motion of the electron along the Z axis is similar to that of the atomic and molecular ions. On the other hand, the magnetic field $\mathbf{B}$ couples the electron’s motion in the X and Y dimension, specifically causing them to undergo cyclotron motion and confining their motion to a cylindrical shell. Then, we determine the electron’s momentum in the XY plane from its radius and polar angle.

It is important to mention that, under standard operating conditions, the magnetic field is not strong enough to affect the ion trajectories and can be neglected. On occasions where a strong magnetic field is used, it may slightly rotate the ion images. This can be

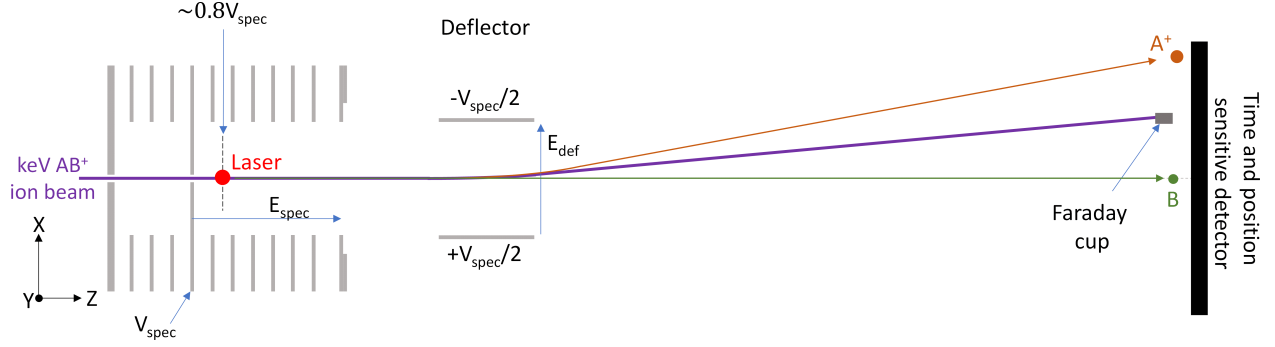


Figure 2.3: *Schematic of the ion beam momentum imaging setup (see text for explanation). Note the figure is not to scale.*

easily corrected for after one precisely determines the strength of the magnetic field from the electron data [9].

2.4 Coincidence momentum imaging of ‘fast’ molecular-ion beams

As previously stated, we also utilize a second coincidence momentum imaging technique to study the fragmentation of “fast” molecular ion beams [11, 41], as shown schematically in Fig. 2.3. The method has been extensively described in our previous group members’ theses [39, 40, 104–107], so we only briefly describe it here.

The molecular ions are produced in an electron cyclotron resonance (ECR) ion source and are accelerated up to 30 keV. We choose the ion energy such that the fragments of interest have sufficient impact energy to be detected efficiently while balancing having 4π solid angle and high-momentum resolution. The ions of interest are separated from other ions produced in the source using a magnet and are collimated using a series of electrostatic quadrupole lenses and four-jaw slits. The beam is steered through the interaction region using electrostatic deflectors with an approximately $1 \times 1 \text{ mm}^2$ cross section.

The laser intersects the ion beam in an electric field approximately parallel to the ion beam’s propagation direction (along the Z axis). This field only extends over a short distance. The laser initiates the dissociation of an arbitrary AB^+ beam into $A^+ + B$, and the

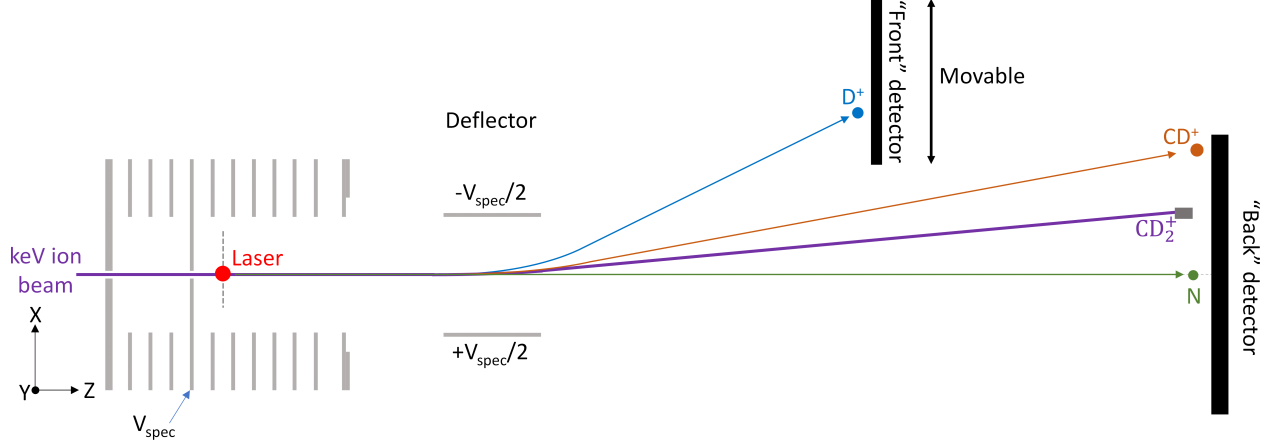


Figure 2.4: *Schematic of the upgraded molecular-ion beam momentum imaging setup with an additional detector to measure the light ionic fragments (see text for explanation). Note the figure is not to scale.*

electric field accelerates the A^+ fragments allowing them to be distinguished in TOF from the neutral B fragments. The resulting fragments traverse a longer field-free region toward the detector, as shown in Fig. 2.3. In some cases, we introduce a second electric field approximately perpendicular to the ion beam’s propagation direction (also shown in Fig. 2.3), which separates the fragments in space based on their charge to energy ratio. Finally, the fragments hit a time and position sensitive detector. From the position and TOF information, we calculate each fragment’s momentum using a similar approach to COLTRIMS, as described in Section 2.3.1. We derive the imaging equations specific to this setup in Appendix A.2. Note that the ion beam is dumped in an approximately 4-mm diameter Faraday cup to monitor its current and to protect the detector.

2.5 Imaging mass asymmetric fragmentation channels

In this section, we briefly present a significant upgrade of our ion-beam imaging method and apparatus to allow us to measure mass asymmetric fragmentation channels in coincidence. The main difficulty of measuring such channels is that the heavy ionic fragments deflect much less than the light fragments, making it challenging to detect both simultaneously [51, 54]. To circumvent this issue, we introduce a second detector to measure the light ionic fragments,

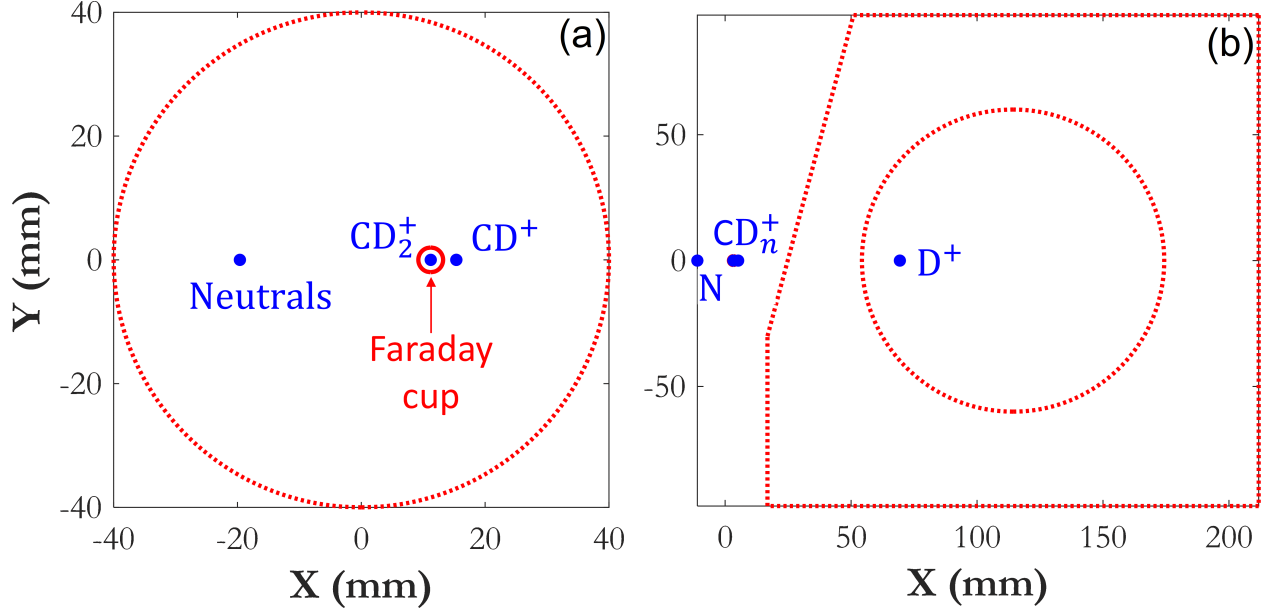


Figure 2.5: The calculated centroids of a CD_2^+ ion-beam’ fragmentation on the (a) back and (b) front detectors. The label N in panel (b) represents the neutral fragments. Note that in this calculation, the ion beam is tuned such that the neutrals hit approximately 20 mm from the center of the back detector and the CD_2^+ beam is deflected about 30 mm from the neutral. It is important to note that the scales of the panels are different.

which we call the “front” detector, located about half-way between the interaction region and the existing detector, named “back”. The schematic of the upgraded experimental setup is shown in Fig. 2.4.

To help illustrate why it is challenging to measure mass asymmetric breakup channels, we consider the fragmentation of the CD_2^+ molecule as an example. For this molecule, it is difficult to simultaneously deflect the center of the CD^+ fragment’s distribution out of the Faraday cup while placing the center of the D^+ fragment’s position distribution on the “back” detector because the light D^+ deflects about seven times further than CD^+ . In Fig. 2.5(a), we show the positions of the Faraday cup and CD^+ fragments when tuning the deflection field to sufficiently remove the CD^+ fragment from the Faraday cup and assuming the ion beam is tuned such that the neutral spot hits approximately 20 mm from the detector’s center. In this configuration, the light D^+ fragment hits approximately 150 mm from the center of the detector, which is far off the detector that has a radius of 40 mm. Therefore, without modifications to the system, we cannot record channels containing the CD^+ and

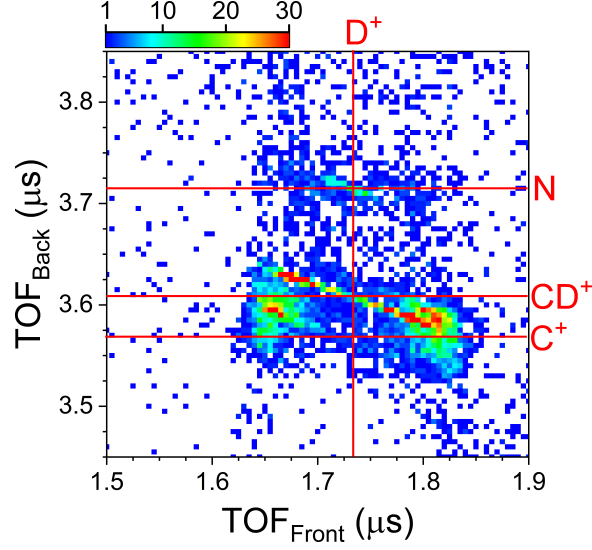


Figure 2.6: The coincidence time-of-flight map for CD_2^+ fragmentation events initiated by an intense laser with peak intensity of about 10^{15} W/cm² where one hit is on the “front” detector and a second hit is on the “back” detector. The red lines represent the expected TOFs for the different fragments on each detector. Note the label N represents the neutral fragments.

D^+ fragments simultaneously, which are important for measuring the competition between hydrogen elimination ($D + CD^+$) and deprotonation ($D + CD^+$).

To measure the light D^+ and heavy CD^+ fragments simultaneously, we place a second time- and position-sensitive detector approximately half the distance between the interaction region and the original detector, as can be seen in Fig. 2.4. The idea is that the light D^+ fragments hit this “front” detector while the heavy ions and neutral fragments fly underneath it and hit the “back” detector, as shown in Fig. 2.5(b). It is important to note that we mounted the “front” detector on a manipulator, allowing one to tune its position along the X-axis. Furthermore, we carefully shielded that detector so that the high voltages needed to operate it do not distort the trajectories of the ions traveling underneath.

Fig. 2.6 shows our first successful measurements using the new two-detector setup. Specifically, we plot the counts as a function of the TOF of hits on the front and back detectors. We observe the dissociation channel $D^+ + CD$, the dissociative ionization channel $D^+ + CD^+$, as well as some three-body channels like $D^+ + D^+ + C^+$. It is important to note that the data analysis is still in its preliminary stages. We are still working on carefully calibrating the

setup to evaluate the correct momenta distributions. We plan to accomplish this in the near future.

We have also performed preliminary measurements on CD_3^+ fragmentation where, like in CD_2^+ , we can study hydrogen elimination versus deprotonation. In the future, we hope to extend such measurements to more complex polyatomic molecules, along with studying four-body fragmentation, as we discuss in Section 3.6. Overall, the upgrade of the experimental setup opens many interesting avenues for studying laser molecular-ion interactions that were previously not feasible in our lab.

Chapter 3

Imaging multi-body sequential fragmentation: native frames analysis

In this chapter, we discuss our results of molecular multi-body sequential fragmentation. Specifically, we introduce a new method for identifying and, in many circumstances, separating three-body sequential breakup from concerted fragmentation. Furthermore, we explore the power of the method with a few examples, its limitations, and then extend it to 4-body fragmentation.

3.1 Background and motivation

In contrast to diatomic molecules, polyatomic molecules offer many additional complexities, such as isomerization [55, 56, 108–113], conical intersections [114–117], and more. This chapter focuses on one such complexity, namely where bonds within the molecule break at different times, which is known as sequential fragmentation [57, 58].

To define sequential and concerted fragmentation, we consider an arbitrary triatomic ABC molecule for simplicity. Specifically, the ABC molecule can absorb a photon and break concertedly, i.e. where all bonds break quickly relative to the vibrational period of the

molecule, leading to



Alternatively, the bonds can break sequentially (i.e. step-wise), for example leading to



where AB^* represents a metastable molecule populated in some state with a long enough lifetime τ . Due to the initial bending normal mode of the ABC molecule and the interaction of the ejected C and AB^* fragments, the intermediate AB^* molecule may begin to rotate, providing researchers with a signature to identify this sequential process.

Although methods exist that can occasionally identify sequential fragmentation from the kinetic energies and lab-frame angular distributions of single fragments [57, 118, 119], the most popular contemporary methods require the coincidence three-dimensional momentum imaging of all fragments [59, 60, 120–122]. Specifically, the modern methods look for correlations (or lack thereof) between fragments due to the rotation of the intermediate molecule [59, 60, 120–122]. The two most widely used methods are the Newton diagram [59, 120] and Dalitz plot¹ [59, 122, 123], shown in Fig. 3.1 for the triple ionization and dissociation of OCS into $O^+ + C^+ + S^+$ ². The dashed lines in the plot trace where sequential fragmentation via the CO^{2+} and CS^{2+} intermediates is expected.

To explain the typical signatures of sequential fragmentation in the Newton diagrams and Dalitz plots, one must first understand the common conditions used to identify the signatures from a classical viewpoint. First, due to momentum conservation³, all measured (i.e. asymptotic) momenta in three-body breakup lie in a plane, called the fragmentation plane. Then, the first condition is that the AB intermediate rotates in this fragmentation

¹Note that Dalitz plots do not require the three-dimensional momentum distributions of the fragments, just their energies.

²Note that this is the same data in the papers we present in Sections 3.2 and 3.4, which were performed in a collaboration of the groups of Itzik Ben-Itzhak, Brett Esry, Artem Rudenko, and Daniel Rolles.

³Recall that all measured momenta are evaluated in the center-of-mass frame of the parent molecular ion.

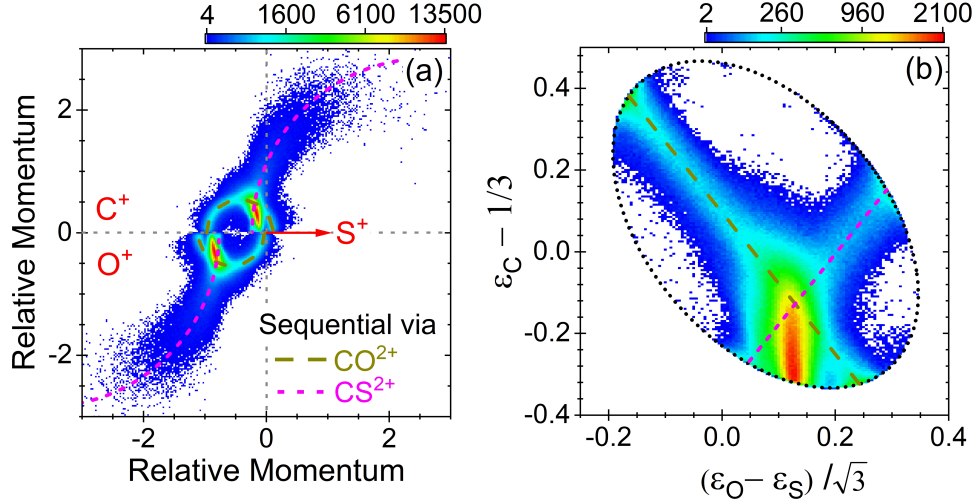


Figure 3.1: (a) The Newton diagram for the strong-field triple ionization and dissociation of OCS into $O^+ + C^+ + S^+$. In this plot, the momentum of the S^+ fragment is rotated to lie along the x axis. The momenta of the C^+ and O^+ are oriented to lie in the top and bottom half of the plot, respectively. Furthermore, their momenta are divided by the magnitude of the S^+ momenta. (b) The Dalitz plot for the same data, where ϵ_j represents the kinetic energy of the j th fragment divided by the total kinetic energy release. The dark yellow and magenta lines represent the contributions of sequential fragmentation via an CO^{2+} and CS^{2+} intermediate, respectively.

plane⁴. The second common condition is that the lifetime of the populated state of the AB^* intermediate molecule is long enough such that it breaks randomly in rotation angle. In other words, the lifetime of the populated state of the metastable AB molecule is much longer than its rotational period [58, 60, 121]. We discuss the implications of these assumptions throughout this chapter.

The Newton diagram is a momentum correlation map of the three fragments. Due to the rotation of the intermediate fragment in the fragmentation plane, sequential fragmentation's signature is an offset semi-circular distribution [59, 120]. In Fig. 3.1(a), we show an example Newton diagram for the strong-field triple ionization and dissociation of OCS into $O^+ + C^+ + S^+$. Specifically, we fix the S^+ momentum to the x axis and rotate the distributions such that the momenta of the C^+ and O^+ fragments lie in the top and bottom half of the plot, respectively. Furthermore, their momenta are scaled by the magnitude of the S^+ momenta.

⁴Note that this condition is not always satisfied. For example, if we begin with a non-planar molecule, the rotation most likely does not occur in the final fragmentation plane, as will be discussed in Section 3.5 for the ammonia molecule

In this plotting scheme, sequential fragmentation via a CO^{2+} intermediate appears as offset semi-circles, as depicted by the dashed dark yellow lines. On the other hand, sequential fragmentation via the CS^{2+} intermediate appears as a “sprinkler”-like feature, indicated by the dashed magenta line. To make sequential breakup via the CS^{2+} intermediate appear as a semi-circular feature, one must create a Newton diagram with the O^+ momentum fixed to the x axis.

The other plotting method for identifying and even partially separating sequential fragmentation is the Dalitz plot [59, 122, 123], shown for the same OCS breakup in Fig. 3.1(b). Specifically, the Dalitz plot displays the energy sharing between the three fragments. Sequential fragmentation’s typical signature in this plot is a distribution following a straight line spanning the range allowed by momentum conservation, where the energy sharing region allowed by momentum conservation is depicted by the black dotted line in Fig. 3.1(b). The signature of sequential fragmentation is a straight line due to the rotation of the intermediate fragment in the fragmentation plane, which forces the final kinetic energies of the intermediate’s fragments in the center of mass of the recoiling parent ion to depend on the intermediate’s rotation angle. In other words, the kinetic energy of a fragment is smaller or larger depending on whether the fragment flies in the opposite or same direction as the intermediate’s center-of-mass momentum, respectively.

Recently, we developed the native-frames analysis [60], which uses the conjugate momenta derived from the Jacobi coordinates to reduce the dimensionality of the data. Then, we can identify and separate sequential from concerted breakup by taking advantage of how the conjugate momenta naturally describe each step of sequential breakup. Specifically, the signature of three body sequential breakup is a uniform distribution as a function of the angle between two conjugate momenta as long as the rotation of the intermediate occurs in the fragmentation plane and the lifetime of the populated rovibrational state is much larger than its rotation period (described in detail in Section 3.4). The advantage of this analysis approach is that one can identify the states responsible for each fragmentation step (see Section 3.3), can separate the competing sequential and concerted fragmentation contributions (Sections 3.2 and 3.4), and extended the analysis to four or more body fragmentation

(Section 3.6).

Finally, it is important to note that the separation of sequential and concerted fragmentation is imperative for the direct study of the molecular dynamics. For example, sequential fragmentation results in the breakdown of the axial recoil approximation [124], i.e. the approximation that the fragments depart along their bond axis. While the axial recoil approximation is not guaranteed to be generally true, it is beneficial to eliminate the most egregious offenders, i.e. sequential fragmentation, when trying to interpret the concerted breakup data that more commonly satisfies the approximation. This is important, for example, in retrieving molecular-frame photoelectron angular distributions [125–130], photofragment angular distributions with respect to the light source’s polarization [131, 132], relative angles between fragments [121, 133], and more.

Native frames analysis also provides researchers with a tool to generally study molecular, and even nuclear, fragmentation dynamics. Specifically, the conjugate momenta provide researchers with a systematic framework for reducing the data’s dimensionality and generalizing to four or more fragments. Overall, we believe native frames can prove to be a powerful tool far beyond just studying sequential fragmentation, which is the focus of the remainder of this chapter.

3.2 Disentangling sequential from concerted fragmentation

This section presents our publication in *Physical Review Letters* that first demonstrated the newly developed native frames method using the strong-field-induced triple ionization and dissociation of OCS molecules as an example. Specifically, we introduce the important concept of the analysis method, that is, using the conjugate momenta derived from Jacobi coordinates to analyze sequential fragmentation. We show that the signature of sequential fragmentation is a uniform distribution of the angle between the conjugate momenta describing the first and second fragmentation steps. Then, using this signature, we confirm

previous studies showing that OCS^{3+} may undergo sequential fragmentation via the CO^{2+} and CS^{2+} intermediate molecules.

We expand on the previous studies by identifying possible rovibrational states of the CO^{2+} intermediate molecule as an example. Identification of the populated states of CS^{2+} are discussed in the follow up paper presented in Section 3.4. In addition, we compare the first step of sequential fragmentation involving the CO^{2+} molecule with its corresponding two-body channel, i.e. $\text{CO}^{2+} + \text{S}^+$, where the metastable CO^{2+} molecule survives its flight to the detector.

Finally, we demonstrate the strength of our method by taking advantage of the uniform angular distribution. Specifically, we show how parts of the sequential fragmentation distribution masked by other competing processes can be reconstructed on an event-by-event basis. Then, using these reconstructed events, we show how the distributions of sequential and concerted breakup can be separated in any plot created from the measured momenta.

A former post-doc, Jyoti Rajput, and I drove this project towards completion. Specifically, my role was to help Jyoti set up the experiment and acquire the data. In addition, I analyzed the data, developed the algorithm for reconstructing the whole sequential fragmentation distribution and for separating sequential from concerted breakup, and interpreted the results for publication. Furthermore, the groups of Artem Rudenko and Daniel Rolles helped acquire the data while Brett Esry gave helpful suggestions, including advising us to use the conjugate momenta of the Jacobi coordinates to analyze the fragmentation processes.

Native Frames: Disentangling Sequential from Concerted Three-Body Fragmentation

Jyoti Rajput,^{*} T. Severt, Ben Berry, Bethany Jochim, Peyman Feizollah, Balram Kaderiya, M. Zohrabi, U. Ablikim, Farzaneh Ziaee, Kanaka Raju P., D. Rolles, A. Rudenko, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak[†]
J. R. Macdonald Laboratory, Physics Department, Kansas State University, Manhattan, Kansas 66506, USA



(Received 18 November 2017; published 8 March 2018)

A key question concerning the three-body fragmentation of polyatomic molecules is the distinction of sequential and concerted mechanisms, i.e., the stepwise or simultaneous cleavage of bonds. Using laser-driven fragmentation of OCS into $O^+ + C^+ + S^+$ and employing coincidence momentum imaging, we demonstrate a novel method that enables the clear separation of sequential and concerted breakup. The separation is accomplished by analyzing the three-body fragmentation in the native frame associated with each step and taking advantage of the rotation of the intermediate molecular fragment, CO^{2+} or CS^{2+} , before its unimolecular dissociation. This native-frame method works for any projectile (electrons, ions, or photons), provides details on each step of the sequential breakup, and enables the retrieval of the relevant spectra for sequential and concerted breakup separately. Specifically, this allows the determination of the branching ratio of all these processes in OCS^{3+} breakup. Moreover, we find that the first step of sequential breakup is tightly aligned along the laser polarization and identify the likely electronic states of the intermediate dication that undergo unimolecular dissociation in the second step. Finally, the separated concerted breakup spectra show clearly that the central carbon atom is preferentially ejected perpendicular to the laser field.

DOI: [10.1103/PhysRevLett.120.103001](https://doi.org/10.1103/PhysRevLett.120.103001)

Advances in imaging techniques have led to a better understanding of molecular fragmentation [1–6]. Experimentally distinguishing between concerted and sequential (sometimes called “stepwise”) fragmentation mechanisms in polyatomic molecules is a long-standing goal of these efforts (see, for example, Refs. [3,5,7–17]). Key to its achievement is the coincidence detection of all fragments, although alternatives without coincidence measurements have been suggested [7]. In recent years, coincidence momentum imaging techniques have progressed significantly toward this goal [5,10–17].

Despite these advances, understanding three-body breakup remains a challenge. For instance, one process that still requires work is the sequential three-body breakup of a triatomic molecule. In the case of a triply charged triatomic molecule, which can be imaged easily, there may be an intermediate step. Of particular interest are metastable intermediate states that survive much longer than their rotational period, i.e., $\tau \gg T_R$. This sequential process has been invoked to explain a circular feature in a Newton diagram showing the momentum correlation of the three final fragments measured in coincidence [5,12–14,16,17]. The same fragmentation mechanism appears as a linear distribution across a Dalitz plot [5,12–16]—a plot depicting the energy sharing among the three fragments [18]. However, neither of these data visualization strategies facilitates complete separation of sequential fragmentation and concerted breakup.

One step towards resolving this problem was taken in a recent study of core-hole localization by Guillemin *et al.* [13]. They managed to partly separate $CS_2^{4+} \rightarrow C^+ + S^+ + S^{2+}$ fragmentation events associated with the sequential or concerted mechanisms. Though the separation was sufficient to address the question of core localization versus delocalization, they stated clearly the limitations of their method, saying “because the disentanglement of the two fragmentation mechanisms is based solely on kinetic energy considerations, this selection is imperfect and both mechanisms can still contribute moderately to the resulting” spectra.

In this work, we demonstrate a more complete way to analyze three-body breakup data that allows us to systematically distinguish sequential fragmentation events as long as the intermediate molecule rotates long enough.

The beauty of the method presented here is that it also allows us to “recover” sequential fragmentation events that are masked by competing processes, and it therefore enables the generation of spectra for concerted breakup events through subtraction of the sequential fragmentation events.

To demonstrate our method, we use the triple ionization of OCS leading to $O^+ + C^+ + S^+$, because two sequential fragmentation routes, proceeding through $S^+ + CO^{2+}$ or $O^+ + CS^{2+}$, have been reported [14]. The events identified with each sequential breakup mechanism reveal essential information that enables one to pinpoint the intermediate states of the diatomic dication as well as the precursor

OCS³⁺ states involved in the dissociation path. Moreover, the separation of these sequential fragmentation channels from each other and from the concerted breakup facilitates branching ratio determination.

In our experiment, the triple ionization of OCS was initiated by intense ($\lesssim 10^{15}$ W/cm²) linearly polarized ($E \parallel Z$) laser pulses centered at 790 nm with 23-fs duration (FWHM in intensity) provided at 10 kHz by one of our lab's lasers, known as PULSAR [19]. The laser was focused on a supersonic jet within a Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) apparatus [20] (see the reviews in Refs. [21–23]), where the time-of-flight (TOF) and position information of each ion is recorded event by event. The primary channel of interest is the fragmentation of OCS³⁺ into O⁺ + C⁺ + S⁺ identified by triple coincidence [24]. We also measured the two-body breakup channels associated with sequential fragmentation, namely, S⁺ + CO²⁺ and O⁺ + CS²⁺, for which the metastable dication's lifetime is longer than its TOF.

The first challenge is to identify which O⁺ + C⁺ + S⁺ events result from sequential fragmentation. Classically, what sets these events apart is that the intermediate molecular fragment rotates long enough to “forget” any alignment imprinted by the first breakup step [5,12–16]. However, instead of using a Newton diagram or Dalitz plot to identify these events, we take advantage of the two-step nature of the process and analyze the data in the two native frames of reference associated with each breakup step. Specifically, we analyze the first step in the OCS³⁺ center-of-mass (c.m.) frame and the second step in the c.m. frame of the intermediate dication, using the relative momenta, shown in Fig. 1(a), defined from the three-body Jacobi coordinates (see, e.g., Refs. [27,28]).

Importantly, the relative direction of the CO²⁺ unimolecular dissociation in the fragmentation plane, denoted by the angle $\theta_{\text{CO},S}$ in Fig. 1(a), is intuitively expected

to be uniform for states that rotate for a long time compared to the rotational period. Since classical calculations indicate that the Coulomb repulsion can impart high angular momentum ($\sim 60\hbar$) to the CO²⁺ [5,29] the relevant rotational period can be considerably shorter than expected for $J = 1$. The calculations also suggest that this rotation occurs in the molecular plane [30].

In cases where such modeling is not feasible, however, we can directly test whether the CO²⁺ rotates in the fragmentation plane using the Euler angles defined in Fig. 1(b). The Euler-angle distributions shown in Fig. 1(c) reveal, for example, that three-body breakup is favored when the laser polarization is in the fragmentation plane, $\cos\beta = 0$. Because of this, the peaks at $\gamma = \pm 90^\circ$ indicate a clear preference for the first breakup step to align with the laser field. Most importantly, though, the flat ridges visible for $\theta_{\text{CO},S} < 100^\circ$ indicate that $N(\theta_{\text{CO},S})$ is constant as expected if the CO²⁺ rotates in the fragmentation plane independently of the plane's alignment. The constant $N(\theta_{\text{CO},S})$ distribution is the signature used to identify sequential breakup events not masked by other competing processes, and it is employed to “recover” concealed sequential events. Notice that although $\theta_{AB,C}$ is a polar angle, $N(\theta_{AB,C})$ is uniform as befits rotation in a plane—the more usual $N(\cos\theta_{AB,C})$ would be isotropic for rotation on a sphere [30].

Another measurable quantity that helps identify sequential fragmentation is the kinetic energy release (KER) in the second step [31,32], i.e., $\text{KER}_{\text{CO}} = p_{\text{CO}}^2/2\mu_{\text{CO}}$, where p_{CO} and μ_{CO} are, respectively, the relative momentum and reduced mass of the C⁺ and O⁺ fragments. Note that KER_{CO} is expected to enable identification of the metastable states of CO²⁺ playing a role.

We plot all the O⁺ + C⁺ + S⁺ events as a function of KER_{CO} and $\theta_{\text{CO},S}$ in Fig. 2(a). The sequential fragmentation proceeding through a CO²⁺ intermediate molecule is clearly identified as the uniform angular distribution centered around 6.5 eV. The dominant concerted breakup channel peaks around $(\text{KER}_{\text{CO}}, \theta_{\text{CO},S}) = (6.3 \text{ eV}, 120^\circ)$ leaving a wide range of $\theta_{\text{CO},S}$ where sequential fragmentation events can be observed as the expected flat $N(\theta_{\text{CO},S})$ distribution. This flat distribution extends over the whole $\theta_{\text{CO},S}$ range and becomes visible again for $\theta_{\text{CO},S}$ approaching 180° as illustrated in Fig. 2(b). We note that the narrow dips in $N(\theta_{\text{CO},S})$ around 0° and 180° are experimental artifacts caused by reduced detection efficiency near the detector center due to a high ion rate of OCS^{q+} and He ions from the carrier gas [30].

The unimolecular dissociation of CO²⁺ occurs mainly by predissociation due to spin-orbit coupling to the repulsive lowest ³Σ[−] state [33] on the microsecond to picosecond time scale, i.e., long after the laser pulse, and yields the KER_{CO} distribution shown in Fig. 2(c). Similar KER spectra have been extensively used to identify possible states of dissociating diatomic molecules (e.g., Refs. [34,35]).

The KER of specific electronic and vibrational states of CO²⁺, shown as thick tick marks in Fig. 2(c), are based on

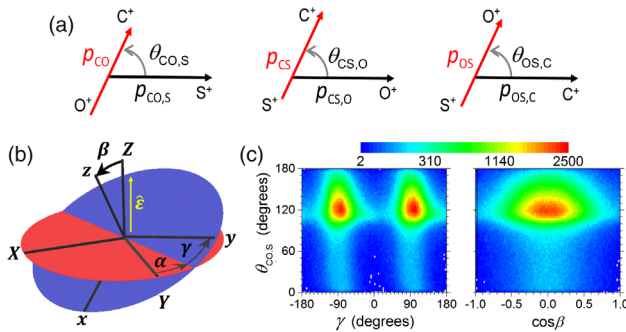


FIG. 1. (a) Relative momenta of three-body breakup, where the black and red arrows represent the first and second breakup steps with the angle $\theta_{AB,C}$ in between—all labeled by the relevant fragments ($\theta_{AB,C}$ is a polar angle in the body frame). (b) The Euler angles [25] of the fragmentation plane (blue) [26] for sequential breakup via CO²⁺ + S⁺. (c) All O⁺ + C⁺ + S⁺ events as a function of $\theta_{\text{CO},S}$ and γ or $\cos\beta$ (integrated over the other angles).

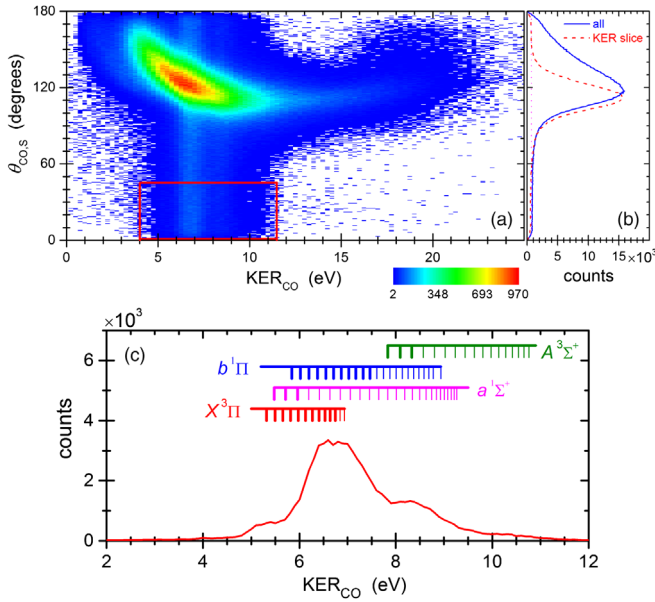


FIG. 2. Sequential breakup of OCS^{3+} via $\text{CO}^{2+} + \text{S}^+$. (a) A density plot of $\text{O}^+ + \text{C}^+ + \text{S}^+$ events as a function of KER_{CO} and $\theta_{\text{CO,S}}$. The gate used to select the sequential breakup events is marked as a red box. (b) The $N(\theta_{\text{CO,S}})$ distributions for all events (solid-blue line) and events within a KER_{CO} slice of 8–11 eV (dashed-red line), matched at the peak. The KER slice indicates that the flat distribution extends to small angles. (c) KER_{CO} distribution of CO^{2+} unimolecular dissociation (step 2) for events within $\theta_{\text{CO,S}} = [0^\circ, 45^\circ]$. The tick marks indicate the expected KER values for field free $J = 1$ states (see text).

high-precision measurements of most of the low-lying metastable states [36], although a few KERs were evaluated using measured vertical photoionization energies [37,38]. We also calculated the KER of higher vibrational states with $J = 1$ (thin tick marks) using the potentials from Ref. [33] and a phase-amplitude method [39]. The possible states can thus be identified by matching the KER values. For example, the peak of the measured KER_{CO} distribution aligns well with the $X^3\Pi(v = 7-12)$ and $b^1\Pi(v = 3-6)$ states, and the low-energy shoulder matches the $a^1\Sigma^+(v = 0-2)$ and $X^3\Pi(v = 0-4)$ states, while the high-KER shoulder may have contributions from the $A^3\Sigma^+(v = 0-3)$ states.

The lifetimes of these states are also crucial to the interpretation of the data, as they must lie between the rotational period and a few-nanosecond maximum imposed by the imaging setup [40]. The relevant rotation period depends on the angular momentum imparted to the CO^{2+} in the first breakup step. Lifetimes calculated including the angular-momentum dependence [41,42] suggest that many of the rovibrational states have lifetimes of the order of 100 ps and therefore can contribute to the KER_{CO} spectrum shown in Fig. 2(c). As an illustration, we calculated predissociation rates for $J = 1$ (see the method in Ref. [43]), which suggest that the $X^3\Pi(v = 2, 5, 8, 9)$ states have the right lifetimes (287, 35.8, 97.7, and 22 ps,

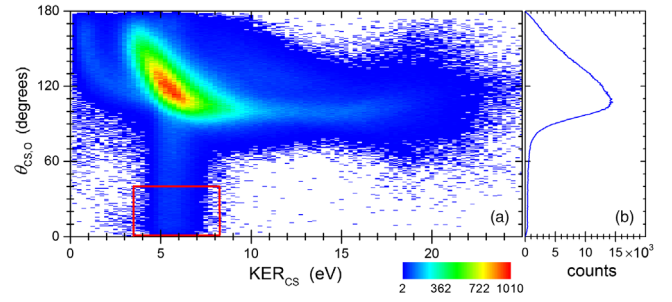


FIG. 3. Sequential breakup of OCS^{3+} via $\text{CS}^{2+} + \text{O}^+$. (a) A density plot of $\text{O}^+ + \text{C}^+ + \text{S}^+$ as a function of KER_{CS} and $\theta_{\text{CS,O}}$. The gate used to select the sequential breakup events is marked by a red box. (b) The $N(\theta_{\text{CS,O}})$ distribution for all events.

respectively) to be key players in the measured sequential fragmentation. In contrast, the lifetime of the $(v, J) = (4, 1)$ state is below 1 ps and therefore may be too short to contribute. Clearly, further work is needed to pinpoint the importance of specific states.

The other sequential fragmentation, involving breakup into $\text{O}^+ + \text{CS}^{2+}$ in the first step, is analyzed similarly. In this case, we plot all $\text{O}^+ + \text{C}^+ + \text{S}^+$ events as a function of KER_{CS} and $\theta_{\text{CS,O}}$ (defined in Fig. 1) in Fig. 3. Here also, a uniform angular distribution is observed for sequential fragmentation events with a CS^{2+} intermediate enabling their selection. Like the other sequential channel, the KER_{CS} distribution and lifetimes of the CS^{2+} states can be used to identify the dissociation path [30].

We return our attention to the first step of the sequential fragmentation and explore its alignment with respect to the laser field, denoted by the angle θ between the polarization and the atomic fragment momentum. The other measurable quantity is the first-step KER [32], given by $\text{KER}_{\text{CO,S}} = p_{\text{CO,S}}^2 / (2\mu_{\text{CO,S}})$, where $1/\mu_{\text{CO,S}} = 1/m_{\text{CO}} + 1/m_{\text{S}}$ and $m_{\text{CO}} = m_{\text{C}} + m_{\text{O}}$, for $\text{S}^+ + \text{CO}^{2+} \rightarrow \text{O}^+ + \text{C}^+ + \text{S}^+$ breakup, with similar expressions for breakup via $\text{O}^+ + \text{CS}^{2+}$.

In Fig. 4 we compare the fragmentation events identified as sequential (three body) to those for which the metastable dication created in step 1 remained intact all the way to the detector (two body). Note the similarity between the final $\text{KER}_{\text{CO,S}} - \cos\theta$ maps of the two- and three-body sequential breakup channels, both tightly aligned along the laser polarization. Interestingly, $\text{KER}_{\text{CO,S}}$ is lower than $\text{KER}_{\text{CS,O}}$ by about 1.33 eV—the energy difference between the two dissociation limits [as demonstrated by the shifted $\text{O}^+ + \text{CS}^{2+}$ distribution (black line) in Fig. 4(c)]. This suggests that both sequential fragmentation channels have the same excitation energy, thus involving the same group of OCS^{3+} potentials.

In addition to the detailed information on sequential fragmentation discussed above, this method allows the determination of the branching ratio of sequential and concerted breakup channels. Taking advantage of the

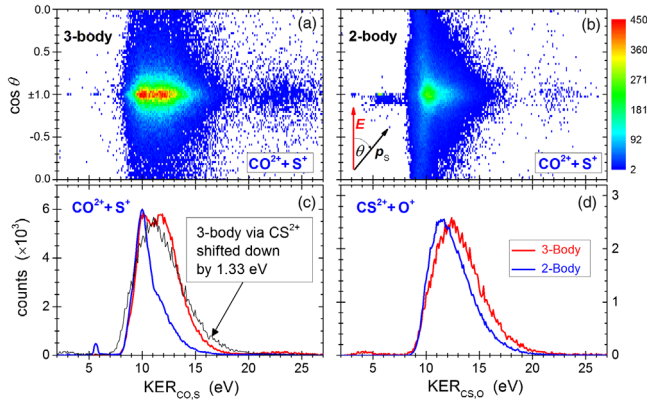


FIG. 4. First step of OCS^{3+} sequential fragmentation. Yield of $\text{CO}^{2+} + \text{S}^+$ as a function of $\text{KER}_{\text{CO,S}}$ and $\cos \theta$ for (a) three-body and (b) two-body breakup. Yield of (c) $\text{CO}^{2+} + \text{S}^+$ and (d) $\text{CS}^{2+} + \text{O}^+$ as a function of the KER (scaled by peak height).

uniform $N(\theta_{\text{CO,S}})$ distribution, the total number of events in each sequential fragmentation channel leading to $\text{O}^+ + \text{C}^+ + \text{S}^+$ is simply given by $[180/(\theta_{\text{max}} - \theta_{\text{min}})] \sum_{\theta_{\text{min}}}^{\theta_{\text{max}}} N(\theta_{\text{CO,S}})$ [44], where $[\theta_{\text{min}}, \theta_{\text{max}}]$ is the gate set on Figs. 2(a) and 3(a). The number of concerted events is then evaluated by subtracting the sequential ones from the total. The branching ratios of the $\text{O}^+ + \text{C}^+ + \text{S}^+$, $\text{S}^+ + \text{CO}^{2+}$, and $\text{O}^+ + \text{CS}^{2+}$ channels in the concerted and first step of sequential breakup are $0.699 \pm 0.007:0.199 \pm 0.008:0.102 \pm 0.006$, respectively. In the second step, $86.9\% \pm 3.7\%$ and $80.0 \pm 5.0\%$ of the CO^{2+} and CS^{2+} , respectively, dissociate while the rest are detected intact in our measurement [30]. One may intuitively attribute the higher fraction of CO^{2+} over CS^{2+} production in step 1 to the “weaker” C–S bond in OCS [45], but that is not sufficient to explain why CO^{2+} production is approximately double that of CS^{2+} . A deeper understanding of the OCS^{3+}

fragmentation in a strong field is needed to address this question.

We now demonstrate a unique additional strength of our native-frames method by separating the different fragmentation channels even where they overlap. This goal is accomplished by taking advantage of the expected flat $N(\theta_{\text{CO,S}})$ distribution of the second fragmentation step when analyzed in the c.m. frame of the intermediate dication. Explicitly, for each event identified as sequential fragmentation with $\theta_{\text{CO,S}}$ within the red “gate” in Fig. 2(a), we create an equivalent event by rotating it to a randomly generated $\theta_{\text{CO,S}}$, $\theta'_{\text{CO,S}}$, outside of the gate. This process is repeated until the distributions outside and inside the gate have the same average value $\overline{N(\theta_r)} = \overline{N(\theta_{\text{CO,S}})}$ (see Ref. [30] for details).

Once a complete set of events for each sequential fragmentation channel is generated, their contributions can be subtracted from any desired spectrum containing all events to yield a separate concerted-breakup spectrum. This is demonstrated by a few examples in Fig. 5 (and Ref. [30]) and the discussion highlighting the information revealed by channel separation.

Newton diagrams for breakup through $\text{S}^+ + \text{CO}^{2+}$ and its separation into the individual fragmentation processes are shown in Figs. 5(a)–5(d). Although diagrams like the one shown in Fig. 5(a) allowed the qualitative identification of sequential fragmentation via the circular feature [5,12–14,16], employing such diagrams for quantitative studies is limited. In contrast, the native-frames method enables channel separation, as shown in Figs. 5(b)–5(d), and the quantitative exploration of the separated channels. We also note in Fig. 5(d) the high-momentum, “sprinklerlike” distribution caused by the other sequential breakup channel.

Finally, the momentum distribution of C^+ fragments in the fragmentation plane is shown in Fig. 5(f) in the

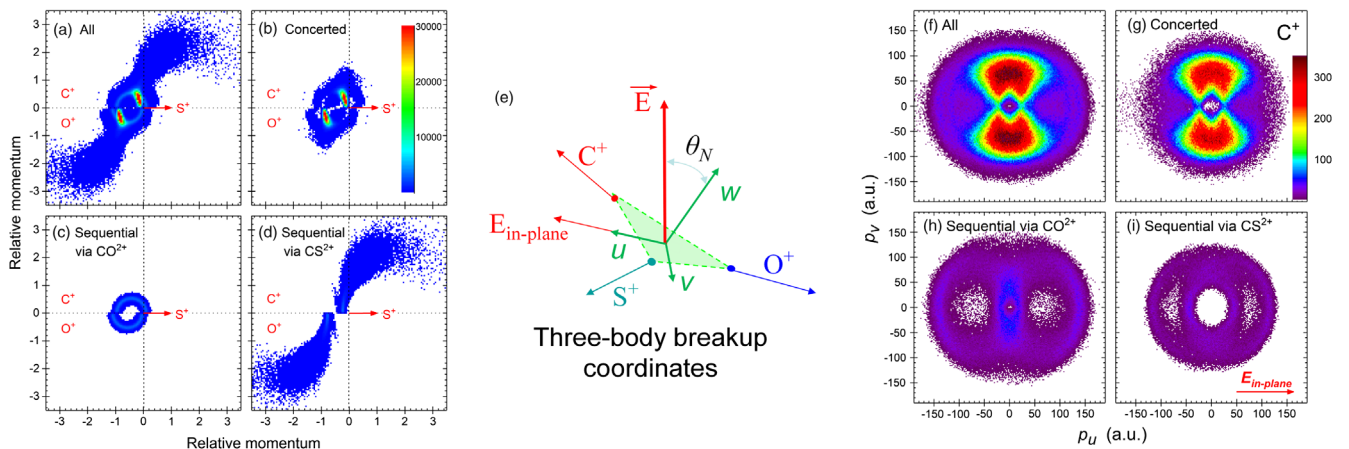


FIG. 5. Channel separation, where “All” denotes all channels together, while “Concerted,” “Sequential via CO^{2+} ,” and “Sequential via CS^{2+} ,” refer to the separate breakup channels, respectively (see text). (a)–(d) Newton diagrams showing relative momenta with respect to S^+ momentum, which is set along the x axis. (e) The u, v three-body fragmentation plane where u is parallel to the polarization projection in this plane. (f)–(i) Momentum distribution of the C^+ fragment in the fragmentation plane.

common way. Subtracting the sequential channels reveals that only the dominant perpendicular component survives [see Fig. 5(g)], clearly indicating that in concerted breakup the central atom of the linear molecule is preferentially ejected perpendicular to the laser field. The “circular” patterns in Figs. 5(h) and 5(i), which complicate the interpretation of the momentum image in Fig. 5(f), are caused by the fact that the fragmentation plane, defined by the relative momenta, is not directly correlated with the laser polarization because the second step occurs long after the laser pulse.

To summarize, we have introduced a powerful native-frames method to analyze three-body breakup, which allows one to identify sequential breakup if the intermediate molecular fragment rotates long enough to generate a uniform angular distribution in its c.m. frame. The key idea is to analyze the coincidence three-dimensional momentum imaging data in the native frame of reference associated with each breakup step and take advantage of the expected uniform $\theta_{AB,C}$ distribution. This method provides detailed information about the two steps of sequential breakup, and it also allows the determination of the branching ratios of the competing breakup mechanisms, which is not easy with other methods.

Significantly, the simplicity of the $KER-\theta_{AB,C}$ distribution facilitates the retrieval of all the sequential fragmentation events including those masked by other breakup channels. This enables their subtraction, allowing the concerted breakup spectra to be isolated.

This powerful method is not limited to the OCS molecule or to laser-driven fragmentation. It should also be applicable to molecular three-body breakup of other charge states, including neutrals, and to more than three fragments. The principle of using the native frame for analysis applies in all these cases and more.

The specific advantages described here, however, require a sequential process in which the intermediate state has an identifiable property, such as sufficient angular momentum to generate a uniform angular distribution, to allow its separation. In the present case—as it will be in most cases—this property is assumed. It is a crucial feature of our method that this assumption can be tested. Specifically, we verify that the intermediate molecular fragment rotates preferentially in the fragmentation plane generating a uniform $\theta_{AB,C}$ distribution that is independent of the alignment of that plane.

We thus expect the native-frames method to benefit future studies of breakup processes as well as the reanalysis of past measurements.

This work is supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy under Award No. DE-FG02-86ER13491.

*Present address: Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India.

†ibi@phys.ksu.edu

- [1] *Imaging in Molecular Dynamics—Technology and applications*, edited by B. Whitaker (Cambridge University Press, New York, 2003).
- [2] *Ten Years of COLTRIMS and Reaction Microscopes*, edited by J. Ullrich (Max-Planck-Institut für Kernphysik Heidelberg, Heidelberg, Germany, 2004).
- [3] U. Werner, K. Beckord, J. Becker, and H. O. Lutz, *Phys. Rev. Lett.* **74**, 1962 (1995).
- [4] A. Hishikawa, A. Iwamae, and K. Yamanouchi, *Phys. Rev. Lett.* **83**, 1127 (1999).
- [5] N. Neumann, D. Hant, L. P. H. Schmidt, J. Titze, T. Jahnke, A. Czasch, M. S. Schöffler, K. Kreidi, O. Jagutzki, H. Schmidt-Böcking, and R. Dörner, *Phys. Rev. Lett.* **104**, 103201 (2010).
- [6] I. Bocharova, R. Karimi, E. F. Penka, J.-P. Brichta, P. Lassonde, X. Fu, J.-C. Kieffer, A. D. Bandrauk, I. Litvinyuk, J. Sanderson, and F. Légaré, *Phys. Rev. Lett.* **107**, 063201 (2011).
- [7] C. E. M. Strauss and P. L. Houston, *J. Chem. Phys.* **94**, 8751 (1990).
- [8] C. Maul and K.-H. Gericke, *Int. Rev. Phys. Chem.* **16**, 1 (1997).
- [9] S. Hsieh and J. H. D. Eland, *J. Phys. B* **30**, 4515 (1997).
- [10] A. Hishikawa, H. Hasegawa, and K. Yamanouchi, *Chem. Phys. Lett.* **361**, 245 (2002).
- [11] J. D. Savee, V. A. Mozhayskiy, J. E. Mann, A. I. Krylov, and R. E. Continetti, *Science* **321**, 826 (2008).
- [12] C. Wu, C. Wu, D. Song, H. Su, Y. Yang, Z. Wu, X. Liu, H. Liu, M. Li, Y. Deng, Y. Liu, L.-Y. Peng, H. Jiang, and Q. Gong, *Phys. Rev. Lett.* **110**, 103601 (2013).
- [13] R. Guillemin, P. Decleva, M. Stener, C. Bommé, T. Marin, L. Journal, T. Marchenko, R. Kushawaha, K. Jänkälä, N. Trcera, K. Bowen, D. Lindle, M. Piancastelli, and M. Simon, *Nat. Commun.* **6**, 6166 (2015).
- [14] B. Wales, È. Bisson, R. Karimi, S. Beaulieu, A. Ramadhan, M. Giguère, Z. Long, W.-K. Liu, J.-C. Kieffer, F. Légaré, and J. Sanderson, *J. Electron Spectrosc. Relat. Phenom.* **195**, 332 (2014).
- [15] A. Ramadhan, B. Wales, R. Karimi, I. Gauthier, M. MacDonald, L. Zuin, and J. Sanderson, *J. Phys. B* **49**, 215602 (2016).
- [16] Z. Shen, E. Wang, M. Gong, X. Shan, and X. Chen, *J. Chem. Phys.* **145**, 234303 (2016).
- [17] X. Ding, M. Haertelt, S. Schlauderer, M. S. Schuurman, A. Y. Naumov, D. M. Villeneuve, A. R. W. McKellar, P. B. Corkum, and A. Staudte, *Phys. Rev. Lett.* **118**, 153001 (2017).
- [18] R. H. Dalitz, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **44**, 1068 (1953).
- [19] X. Ren, A. M. Summers, Kanaka Raju P., A. Vajdi, V. Makhija, C. W. Fehrenbach, N. G. Kling, K. J. Betsch, Z. Wang, M. F. Kling, K. D. Carnes, I. Ben-Itzhak, C. Trallero-Herrero, and V. Kumarappan, *J. Opt.* **19**, 124017 (2017).
- [20] C. M. Maharjan, Ph.D. thesis, Kansas State University, 2007.
- [21] J. Ullrich, R. Moshhammer, R. Dörner, O. Jagutzki, V. Mergel, H. Schmidt-Böcking, and L. Spielberger, *J. Phys. B* **30**, 2917 (1997).

- [22] R. Dörner, V. Mergel, O. Jagutzki, L. Spielberger, J. Ullrich, R. Moshhammer, and H. Schmidt-Böcking, *Phys. Rep.* **330**, 95 (2000).
- [23] J. Ullrich, R. Moshhammer, A. Dorn, R. Dörner, L. P. H. Schmidt, and H. Schmidt-Böcking, *Rep. Prog. Phys.* **66**, 1463 (2003).
- [24] This multiphoton ionization is assumed to be rapid, and the role of metastable autoionizing states to be negligible.
- [25] E. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1998).
- [26] The normal to the fragmentation plane is given by $\hat{z} = \mathbf{p}_{\text{CO},s} \times \mathbf{p}_{\text{CO}} / |\mathbf{p}_{\text{CO},s} \times \mathbf{p}_{\text{CO}}|$, and $\hat{y} = \mathbf{p}_{\text{CO}} / |\mathbf{p}_{\text{CO}}|$.
- [27] C. D. Lin, *Phys. Rep.* **257**, 1 (1995).
- [28] Y. Wang, Ph.D. thesis, Kansas State University, 2010.
- [29] The sensitivity of the $N(\theta_{\text{CO},s})$ distribution to the J states composing the rotational wave packet and their lifetimes is under investigation.
- [30] T. Severt, J. Rajput, B. Berry, B. Jochim, P. Feizollah, B. Kaderiya, M. Zohrabi, U. Ablikim, F. Ziaee, Kanaka-Raju P., D. Rolles, A. Rudenko, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak (to be published).
- [31] A. Khan, L. C. Tribedi, and D. Misra, *Phys. Rev. A* **92**, 030701 (2015).
- [32] S. Yan, X. L. Zhu, P. Zhang, X. Ma, W. T. Feng, Y. Gao, S. Xu, Q. S. Zhao, S. F. Zhang, D. L. Guo, D. M. Zhao, R. T. Zhang, Z. K. Huang, H. B. Wang, and X. J. Zhang, *Phys. Rev. A* **94**, 032708 (2016).
- [33] T. Šedivcová, P. R. Žďánská, V. Špirko, and J. Fišer, *J. Chem. Phys.* **124**, 214303 (2006).
- [34] A. K. Edwards, R. M. Wood, and M. F. Steuer, *Phys. Rev. A* **16**, 1385 (1977).
- [35] See D. Mathur, *Phys. Rep.* **391**, 1 (2004), and references therein.
- [36] M. Lundqvist, P. Baltzer, D. Edvardsson, L. Karlsson, and B. Wannberg, *Phys. Rev. Lett.* **75**, 1058 (1995).
- [37] G. Dawber, A. G. McConkey, L. Avaldi, M. A. MacDonald, G. C. King, and R. I. Hall, *J. Phys. B* **27**, 2191 (1994).
- [38] M. Hochlaf, R. I. Hall, F. Penent, H. Kjeldsen, P. Lablanquie, M. Lavollée, and J. H. D. Eland, *Chem. Phys.* **207**, 159 (1996).
- [39] E. Y. Sidky and I. Ben-Itzhak, *Phys. Rev. A* **60**, 3586 (1999).
- [40] B. Jochim, R. Erdwien, Y. Malakar, T. Severt, B. Berry, P. Feizollah, J. Rajput, B. Kaderiya, W. L. Pearson, K. D. Carnes, A. Rudenko, and I. Ben-Itzhak, *New J. Phys.* **19**, 103006 (2017).
- [41] T. Šedivcová-Uhlková, P. R. Kaprálová-Žďánská, and V. Špirko, *Int. J. Quantum Chem.* **107**, 2654 (2007).
- [42] F. Mrugała, *J. Chem. Phys.* **129**, 064314 (2008).
- [43] J. P. Bouhnik, I. Gertner, B. Rosner, Z. Amitay, O. Heber, D. Zajfman, E. Y. Sidky, and I. Ben-Itzhak, *Phys. Rev. A* **63**, 032509 (2001).
- [44] A small correction due to the dips around $\theta_{\text{CO},s} = 0$ and 180° deg is needed as detailed in Ref. [30].
- [45] W. Kedzierski, J. Borbely, and J. W. McConkey, *J. Phys. B* **34**, 4027 (2001).

3.3 Imaging sequential fragmentation step-by-step and state-selectively

Here, we present a draft of a paper which extends the native-frames analysis to the study of single-photon double ionization of D_2O , where we follow sequential fragmentation step-by-step and state-selectively. In this experiment, we measure the two emitted electrons and both D^+ fragments in coincidence and then calculate the momentum of the neutral O fragment using momentum conservation, as discussed in Section 2.3.2, making this measurement effectively kinematically complete. In this project, we exploit certain advantages that single-photon double ionization has over double ionization induced by intense laser fields, i.e. multiphoton absorption.

In Fig. 3.2, we show schematic cuts of the potential energy surfaces of the neutral, cation, and dication of an arbitrary H_2A molecule. Specifically, the curves are along the asymmetric stretch coordinate R_{AH} , where R_{AH} and bond-angle θ are held constant. The coordinates color-coding and bond angle are defined in Fig. 3.2(a). Furthermore, Figs. 3.2(a) and (b) show example fragmentation pathways following multiphoton dissociative double ionization by an intense laser field and single-photon double ionization, respectively.

In the multiphoton case shown in Fig. 3.2(a), the dynamics are initiated when the H_2A molecule absorbs many photons, transitions to some cationic electronic state, and begins to stretch. At a later time within the laser pulse, the molecule is further ionized by absorbing additional photons and then dissociates into $\text{H}^+ + \text{AH}^+$. The difficulty with interpreting multiphoton absorption-induced fragmentation is that this pathway can also compete with many other pathways not shown here, such as the direct double ionization pathway where many photons are absorbed, transitioning the H_2A molecule straight to the dicationic state before the molecule has time to stretch, or through double ionization via the inelastic rescattering of the initially ejected photoelectron. Furthermore, the measured electron kinetic energies are not as useful in this case because the net number of photons absorbed by the molecule is not known, and the electron energies can be modified by the intense field after ionization,

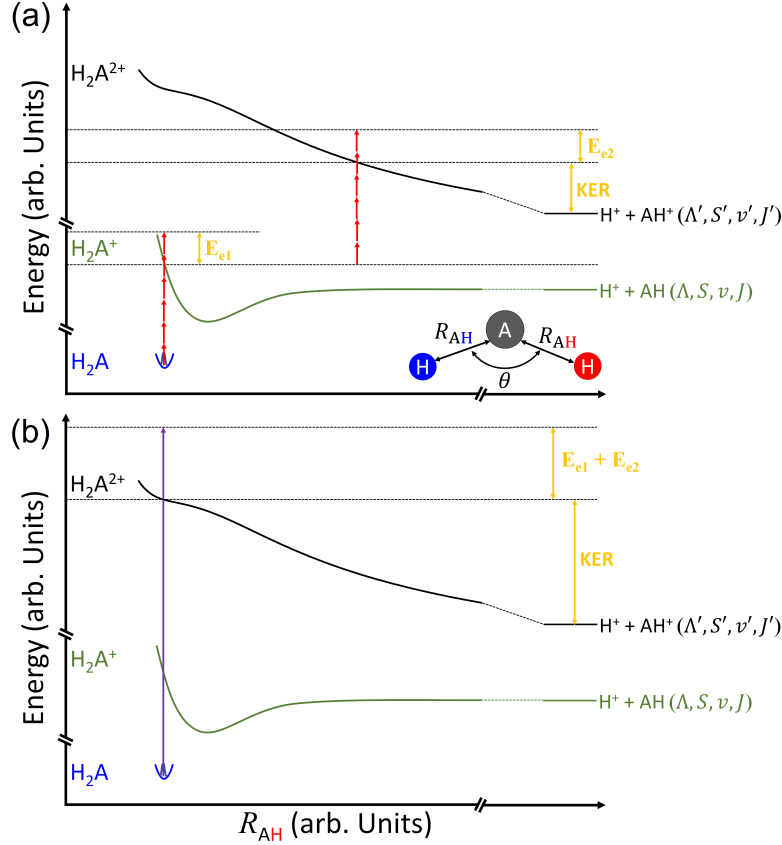


Figure 3.2: *The schematic potential energy curves for the cationic and dicationic states of an arbitrary H_2A molecule. Specifically, (a) shows a possible pathway induced by multiphoton absorption from an ultrafast and intense laser pulse while (b) shows a possible pathway following single-photon double-ionization.*

as in electron rescattering physics [1, 2]. Because other electronic states may lead to many more competing pathways, it is difficult to nail down state-selective dynamics with certainty.

In contrast, the monocationic states are bypassed during single-photon double ionization and can therefore be ignored, as shown in Fig. 3.2(b). Furthermore, we know precisely how much energy is deposited in the system, at least within the bandwidth of the pulse which is ± 50 meV in our experiments. Then, the electrons' kinetic energy sum $E_{e1} + E_{e2}$ provides information about the amount of energy absorbed in excess of the populated electronic state. In other words, this energy identifies the electronic state the dynamics start on. Furthermore, as is generally the case, the energy difference between where the dynamics start and the dissociation limit is the measured kinetic energy release (KER) during fragmentation. Then, the sum of the KER and electron kinetic energies as well as the photon energy can

be used to identify the asymptotic limit where the dynamics end. By determining where the dynamics begin and end, we can establish the dissociation pathways better than with multiphoton absorption in strong laser fields because the number of possible competing pathways is significantly reduced.

In the following paper, we exploit the advantages of single-photon double-ionization explained above. We experimentally track the step-by-step and state-selective sequential fragmentation dynamics of D_2O^{2+} breakup into $\text{D}^+ + \text{OD}^+$, where the OD^+ later breaks into $\text{D}^+ + \text{O}$. Specifically, we explain how to extend native frames to molecules with identical fragments. Furthermore, we identify the D_2O^{2+} states initially populated following the absorption of a 61-eV photon as well as the states of the intermediate metastable OD^+ molecule populated after the first fragmentation step. We also demonstrate that our analysis allows one to accurately measure the internal energy of the OD^+ intermediate that is in excess of the final dissociation limit. In addition, our theoretical results display good quantitative agreement with the experimental data and provide insight about the rotational population of the intermediate molecule. Using both theory and experiment, we show that the intermediate's rotational population is imprinted in the threshold behavior of the kinetic energy release by the OD^+ intermediate due to the shifting of the centrifugal barrier.

This project is a collaboration between our group here at Kansas State University and the AMO research group at Lawrence Berkeley National Lab (LBNL), led by Thorsten Weber on the experimental side and Bill McCurdy on the theory side. This experiment was initiated, in part, following our previous analysis of some lower statistics H_2O data where we identified sequential fragmentation. My main contributions to this paper are the analysis of sequential fragmentation in the higher statistics D_2O data as well as determining how to identify and separate the states contributing to sequential fragmentation. Furthermore, I assisted with the preparation of the manuscript.

Step-by-step, state-selective tracking of sequential fragmentation dynamics of water dications by momentum imaging

Travis Severt^{a,1}, Zachary L. Streeter^{b,c,1}, Wael Iskandar^{b,1}, Kirk A. Larsen^{d,b}, Averell Gatton^{b,e}, Daniel Trabert^f, Bethany Jochim^a, Brandon Griffin^{b,g}, Elio G. Champenois^{d,b}, Matthew M. Brister^b, Dylan Reedy^g, Demetri Call^g, Richard Strom^{b,e}, Allen L. Landers^e, Reinhard Dörner^f, Joshua B. Williams^g, Daniel S. Slaughter^b, Robert R. Lucchese^b, Thorsten Weber^b, C. William McCurdy^{b,c}, and Itzik Ben-Itzhak^{a,2}

^aJ. R. Macdonald Laboratory, Physics Department, Kansas State University, Manhattan, Kansas 66506, USA; ^bChemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA; ^cDepartment of Chemistry, University of California, Davis, California 95616, USA; ^dGraduate Group in Applied Science and Technology, University of California, Berkeley, California 94720, USA; ^eDepartment of Physics, Auburn University, Alabama 36849, USA; ^fInstitut für Kernphysik, Goethe-Universität, Max-von-Laue-Straße 1 60438 Frankfurt am Main, Germany; ^gDepartment of Physics, University of Nevada Reno, Reno, Nevada 89557, USA

This manuscript was compiled on June 4, 2021

We study the sequential fragmentation of heavy water following double ionization by a single photon, and leading to $D^+ + D^+ + O(^3P)$ final products. A combined experimental and theoretical methodology is introduced that enables the identification and separation of the sequential breakup events, via a $D^+ + OD^+$ intermediate, from other processes leading to the same final products. Moreover, we experimentally identify, separate, and follow step by step, two sequential pathways involving the $b^1\Sigma^+$ and $a^1\Delta$ states of the intermediate OD^+ ion. Our classical trajectory calculations on the relevant potential energy surfaces reproduce well the measured data, and combined with the experiment, enable the determination of the internal energy and angular momentum distribution of the OD^+ intermediate.

Coincidence momentum imaging | Photoionization | Sequential fragmentation | Native frames |

The measurement of reaction dynamics occurring on the femtosecond time scale has long been the target of various kinds of time-resolved spectroscopies, and more recently has been accomplished with ultrafast X-ray measurements. Those measurements have exploited pump/probe strategies (1), transient absorption (2) and time-resolved X-ray scattering (3), among other methods. Combining time-resolved X-ray measurements with momentum imaging coincidence detection (4–6) that gives direct access to ionization and dissociation dynamics in the molecular frame remains a challenge.

Although it would seem intuitive that time-resolution is necessary to see the steps in the unimolecular reactions that have frequently been the subjects of momentum imaging coincidence experiments, it was demonstrated recently that such experiments, without time-resolved X-ray or laser pulses, can in fact be used to detect the steps in a sequential reaction (7–15). Recently, the “native-frames analysis” was introduced (15, 16), and the authors showed that photo-induced momentum imaging observations can resolve the sequence of events in the dissociation of a molecule involving vibrational and rotational dynamics following multiple ionization.

Here, we take a step further by combining such measurements with detailed *ab initio* theoretical calculations of the multiple Born-Oppenheimer potential surfaces governing such a reaction and the nuclear dynamics on those surfaces. With this methodology, the spectral signatures of the steps of a reaction, including nonadiabatic transitions that occur in those steps, can be identified in the experimental measurements.

The result is a clear picture, not only of the steps, but of the electronic states involved in them.

We follow sequential fragmentation step-by-step, by combining a kinematically complete measurement of all reaction products following single-photon absorption, computing the classical trajectories on the relevant potential-energy surfaces, and employing the native-frames analysis to separate the measured data into the steps of the process. Moreover, we manage to observe the internal-energy distribution of the intermediate molecule, which has sufficient energy to predissociate.

Our test-case system is the heavy water molecule that fragments into $D^+ + D^+ + O(^3P) + 2e^-$ following the absorption of a single photon. We focus on sequential fragmentation via an OD^+ intermediate, which follows the steps listed below



Note that the D^+ fragments are labeled red and blue according to their ejection order in the sequential process (a notation

Significance Statement

The double photoionization of a molecule by one photon ejects two electrons and typically creates an unstable dication. Observing the subsequent fragmentation products in coincidence can reveal a surprisingly detailed picture of the decay mechanisms. Here, we measure the dynamics of two sequential breakup pathways of D_2O^{2+} , producing a neutral oxygen atom and two deuterons. Comparing the experimentally measured fragments' momenta, expressed using the “native frame” coordinates tailored to the specific sequential mechanism, with *ab initio* theoretical calculations reveals the sub-picosecond first step sequential fragmentation dynamics of a triatomic molecule. The electronic states, vibrational energy, and rotational angular momentum of the transient OD^+ fragment are then determined.

Author contributions: W.I., T.S., K.A. L., D. C., A. G., D. T., B. G., D. R., R. S., E.G. C., B. J., M.M. B., I. B.-I., D.S. S., T. W. Plan, set up, and perform the experiment; T. S. and W. I. conducted the “native frames” and COLTRIMS data analysis, respectively; Z.L. S., R.R. L. perform calculations; J.B. W., A. L., D.S. S., T. W., C.W. McC., I. B.-I. mentor students and post-docs; T. S., Z.L. S., T. W., R.R. L. C.W. McC., and I. B.-I. prepare manuscript, all co-authors approve manuscript.

The authors declare no conflicts of interest.

¹ Travis Severt, Zachary Streeter, and Wael Iskandar, contributed equally by leading the data analysis, theoretical, and experimental aspects of the ALS campaign, respectively.

²To whom correspondence should be addressed. E-mail: ibi@phys.ksu.edu

used throughout). Despite the fact that these D atoms are identical particles, we show below that the sequential breakup step, i.e. the ejection order, can be associated with each detected D^+ fragment.

It was suggested by Streeter *et al.* (17), who identified many measured concerted fragmentation paths in H_2O (18), that one of the reaction pathways leading to the $H^+ + H^+ + O(^3P)$ final state involves sequential breakup via an OH^+ intermediate. Specifically, they speculated that a feature in the data, having broad angular spread between the protons' ejection direction, may be due to transitions involving the 2^1A_1 state of the water dication, which undergoes two-body breakup to $H^+ + OH^+(b^1\Sigma^+)$. This $(b^1\Sigma^+)$ state of OH^+ is known to predissociate into $H^+ + O(^3P)$ via a crossing with the $A^3\Pi$ state (19, 20). In the present work, we validate the sequential-breakup path described above and identify an unexpected additional sequential fragmentation pathway of D_2O^{2+} . Moreover, we reveal details on each step of these stepwise reaction dynamics, and also measure the excess internal energy above the dissociation limit of the metastable intermediate molecule — demonstrating the power of the presented methodology.

Methodology

The methodology that enables us to compare theory and experiment step by step and state selectively is based on three main components, described briefly below. Further details are provided in the references.

Experimental method. First, a kinematically complete experiment is required, and that entails the determination of the final momenta of all fragments from each molecule. In the present case, we measure all the charged fragments in coincidence and determine their final momenta using a cold target recoil ion momentum spectroscopy (COLTRIMS) technique (4–6). Specifically, we focus on events producing two electrons, two deuterons, and a neutral oxygen whose final momentum is evaluated using momentum conservation. To avoid artifacts caused by the identical D^+ fragments, we follow the common practice and randomize their time order, i.e. flip the order of the 1st and 2nd D^+ hits randomly for half of the events.

It is also essential to know how much energy is deposited in each water molecule. To accomplish that we initiate the fragmentation by single-photon absorption, using a 61 eV narrow bandwidth (50 meV) synchrotron light pulse provided by the Advanced Light Source (ALS), thereby producing a doubly-ionized water molecule 24.1 eV above the $D^+ + D^+ + O(^3P)$ dissociation limit. Using this photon energy together with the measured kinetic energy of both electrons and all the other fragments allows the selection of only events ending on the dissociation limit mentioned above (17, 18).

Heavy water, D_2O , is chosen over H_2O in order to circumvent contributions from double ionization of H_2O and H_2 molecules, both common residual gas in ultra high vacuum systems, also producing $H^+ + H^+ + 2e^-$. These residual gases are much warmer than the COLTRIMS jet, and are present throughout the light-beam propagation direction, therefore contaminating the momentum imaging, especially when one cannot use momentum conservation to eliminate them, as is the case for the breakup channel of interest. The D_2O target choice should not affect the fragmentation pathways since each water isotopologue is expected to undergo similar dynamics.

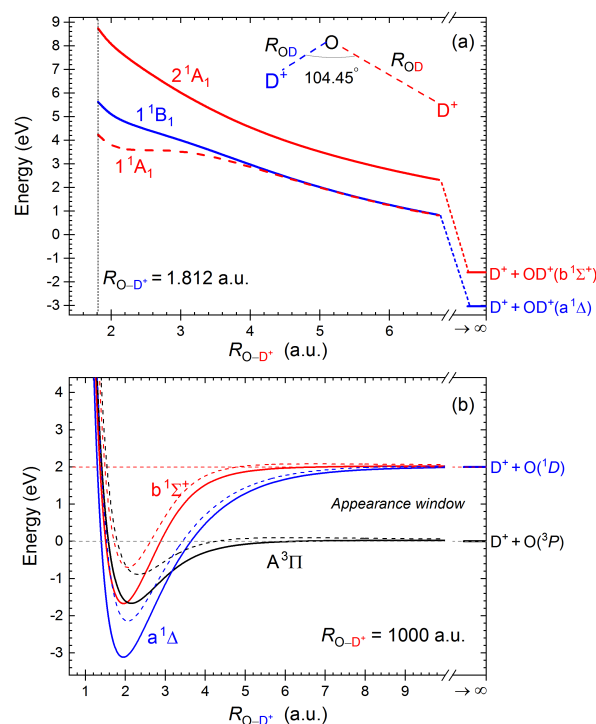


Fig. 1. The relevant potential energy surface for sequential fragmentation of water dications via OD^+ intermediate: Cut through the potential energy surfaces showing (a) the asymmetric stretch of D_2O^{2+} for a fixed bond angle (104.45°) and internuclear distance (1.812 bohr) of the other O–D bond for the three states of D_2O^{2+} that produce the diatomic intermediate which further dissociates (see text), and (b) the OD^+ potentials when the interaction with the other D^+ is negligible (solid and dashed lines are for $J=0$ and $J=30$, respectively). The states in (a) plotted as solid blue and solid red curves produce the diatomic ion with enough internal energy to predissociate via the $A^3\Pi$ state. The energy scale is relative to the $D^+ + D^+ + O(^3P)$ dissociation limit. Note that on this energy scale the asymmetric stretch limits for the 1^1B_1 and 2^1A_1 states in panel (a) are -3.021 and -1.619 eV, respectively.

Theory. The potential energy surfaces of the water dications are computed, using the MOLPRO (21, 22) quantum chemistry suite in internally contracted multireference configuration interaction (icMRCI) methods at the configuration interaction singles and doubles (CISD) level including Davidson correction to the energy, by Gervais *et al.* (20) and Streeter *et al.* (17). The full dimensional surfaces are then fitted using a functional form developed by Gervais *et al.* (20). Those studies established the branching ratios between two-body ($D^+ + OD^+$) and three-body ($D^+ + D^+ + O$) breakup on each potential surface of the nine states of the water dication that can be accessed at the photon energy used in our experiment.

The first step in sequential breakup requires one O–D bond to break, while the OD^+ fragment left behind remains bound. In Fig. 1(a) we show the asymmetric stretch of D_2O^{2+} leading to $D^+ + OD^+$ breakup, specifically cuts in a few potential energy surfaces (PES) computed for a bond angle of 104.45° while holding the other O–D internuclear distance at 1.812 a.u. — both are equilibrium values of D_2O . Figure 1(b) displays cuts in a few PES of D_2O^{2+} for the same bond angle, but when one D^+ is at 1000 a.u. and therefore its interaction with the remaining OD^+ is negligible. This is effectively a plot of the OD^+ states correlating with the $D^+ + O(^3P)$ and $D^+ + O(^1D)$ dissociation limits, which are involved in the predissociation of the intermediate OD^+ molecule.

Using the PES information detailed above, we model the reaction dynamics by the propagation of ensembles of classical trajectories on the relevant potential surface for a few picoseconds, at which time the OD^+ population is evaluated. The computational approach used is the same as that of our previous study (17). The molecule is initially in its ground vibrational state and undergoes a Franck-Condon transition to the doubly ionized excited state. The initial conditions for the 1,000,000 computed classical trajectories, for each D_2O^{2+} state we consider, are sampled from the corresponding Wigner distribution, assuming that the ground vibrational state can be represented by direct product wave function of the normal modes. At the end of the propagation the internal energy, and the rotational angular momentum, J , of the OD^+ fragment are computed from the cartesian momenta and coordinates of the atoms together with the value of the potential energy. The OD^+ is considered to be bound if the total energy of an $\text{O}-\text{D}^+$ pair is less than the J -dependent barrier to dissociation associated with the relevant final states of OD^+ , specifically the $\text{D}^+ + \text{O}(^1D)$ limit shown in Fig. 1(b).

The essence of the second step of the sequential fragmentation is the dissociation of the OD^+ ion produced in the first step in its $\text{b}^1\Sigma^+$ and $\text{a}^1\Delta$ states by a nonadiabatic transition to the $\text{A}^3\Pi$ state mediated by spin-orbit coupling. If the OD^+ ion is produced vibrationally (and rotationally) excited to energies above the dissociation limit of the $\text{A}^3\Pi$ state shown in Fig. 1(b), it can be predissociated by this nonadiabatic transition. The central dynamical assumption of our treatment takes advantage of the relatively short lifetimes for this predissociation via a nonadiabatic transition to the $\text{A}^3\Pi$ state compared to the fragments' flight time in the experimental setup. We therefore assume in our classical trajectory calculations that all OD^+ ions, with internal energy above the $\text{D}^+ + \text{O}(^3P)$ dissociation limit, predissociate within a few picoseconds due to spin-orbit coupling with the $\text{A}^3\Pi$ state (19, 20).

Thus, for example, all trajectories with vibrational energy in the $\text{b}^1\Sigma^+$ state having zero rotational angular momentum and with vibrational energies between the two horizontal dashed lines in Fig. 1(b) labeled "appearance window" are assumed to lead to $\text{D}^+ + \text{O}$ fragments. Such an "appearance window" was recently found to play an important role in another polyatomic molecule, i.e. in the valence photo-double ionization of ammonia (23). Nonzero rotational angular momentum adds a centrifugal barrier to this picture for all three states of OD^+ in Fig. 1(b), modifying the "appearance window", and leaving a clear signature of rotational excitation in the kinetic energy of the atomic fragments produced by this mechanism, as we discuss below. Tunneling through the centrifugal barrier for $J \neq 0$ is neglected in this treatment. Three states of D_2O^{2+} , the 1^1A_1 , 2^1A_1 , and 1^1B_1 states, shown in Fig. 1(a), produce the $\text{b}^1\Sigma^+$ state (which correlates with the 2^1A_1 state) and the two components of the degenerate $\text{a}^1\Delta$ state of OD^+ (19, 20). However only two of those, the 2^1A_1 , and 1^1B_1 states, produce the diatomic ion with enough internal energy to dissociate appreciably by this mechanism and be seen in one-photon double photoionization, as is suggested by Figure 5 of reference (20).

Native frames analysis. Three-body breakup can be analysed using the conjugate momenta of the Jacobi coordinates, where the coordinates describe the relative positions of the three fragments. This is the key ingredient of the "native frames" method (15, 16). In our present case, shown schematically

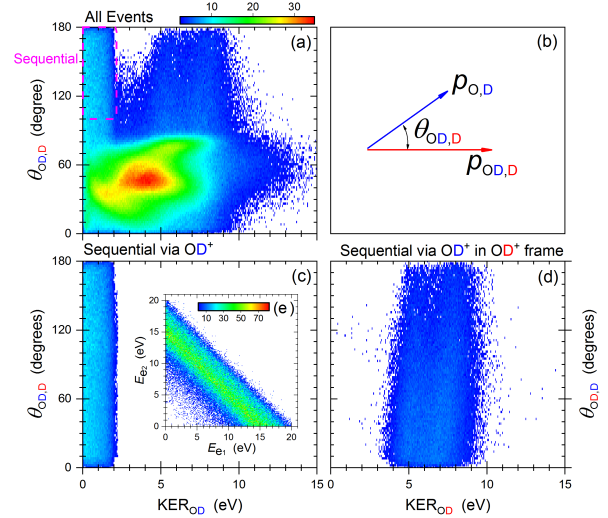


Fig. 2. Native frames analysis of $\text{D}^+ + \text{D}^+ + \text{O}$ breakup (see text). (a) All the measured $\text{D}^+ + \text{D}^+ + \text{O}$ events as a function of the kinetic energy released upon OD^+ dissociation, KER_{OD} , and the angle between the relative momenta, $\theta_{\text{OD},\text{D}}$. Sequential fragmentation events via $\text{D}^+ + \text{OD}^+$ are identified (see text) by the uniform angular distribution within the red-dashed rectangle (i.e., $\text{KER}_{\text{OD}} < 2.3$ eV and $100^\circ < \theta_{\text{OD},\text{D}} < 180^\circ$). (b) Schematic diagram of the relative momenta and the angle between them. Sequential breakup via OD^+ analyzed in the (c) OD^+ and (d) OD^+ frames, i.e., the correct and wrong fragmentation-step order of the D^+ fragments, respectively (see text). Note that analysis of the events in the wrong reference frames, as is the case shown in panel (d) and indicated by the different axis labels (KER_{OD} and $\theta_{\text{OD},\text{D}}$), yields a distribution significantly different than the one expected for sequential fragmentation (15), specifically, a non-uniform angular distribution, a KER_{OD} that depends on the angle $\theta_{\text{OD},\text{D}}$, and a much higher than expected KER_{OD} . (e) Energy-correlation map of the ionized electrons associated with this sequential fragmentation.

in Fig. 2(b), the relative momentum associated with the first fragmentation step is given by

$$\mathbf{p}_{\text{OD},\text{D}} = \frac{m_{\text{OD}}}{M} \mathbf{P}_{\text{D}} - \frac{m_{\text{D}}}{M} [\mathbf{P}_{\text{D}} + \mathbf{P}_{\text{O}}], \quad [2]$$

where $\mathbf{P}_{\text{D}}$ and $\mathbf{P}_{\text{O}}$ are the measured momenta of the D^+ and O fragments, respectively, m_{D} is the mass of D^+ , m_{OD} is the mass of OD^+ , and M is the mass of the D_2O^{2+} .

Similarly, the relative momentum associated with the second step is

$$\mathbf{p}_{\text{OD}} = \mu_{\text{OD}} \left[\frac{\mathbf{P}_{\text{O}}}{m_{\text{O}}} - \frac{\mathbf{P}_{\text{D}}}{m_{\text{D}}} \right], \quad [3]$$

where μ_{OD} is the reduced mass of OD^+ . Finally, the angle between the two relative momenta, $\theta_{\text{OD},\text{D}}$, is computed from the dot product of these vectors. Equations (2) and (3) are the conjugate momenta of the Jacobi coordinates for the $\text{D} + \text{OD}$ arrangement.

The second ingredient needed to separate sequential fragmentation is a clear signature distinguishing it from other fragmentation processes. Rotation of the intermediate diatomic ion in the fragmentation plane provides such a signature (9–12, 15, 16, 24). In the native frames analysis this rotation manifests itself as a nearly uniform $N(\theta_{\text{OD},\text{D}})$ angular distribution if the predissociation lifetime is long enough so the rotation of OD^+ wipes out any initial angular preference. The kinetic energy release (KER) in the second fragmentation step combined with molecular structure of the intermediate molecule provides an additional constraint for identifying sequential breakup. To that end, we plot in Fig. 2(a) all the measured $\text{D}^+ + \text{D}^+ + \text{O}$

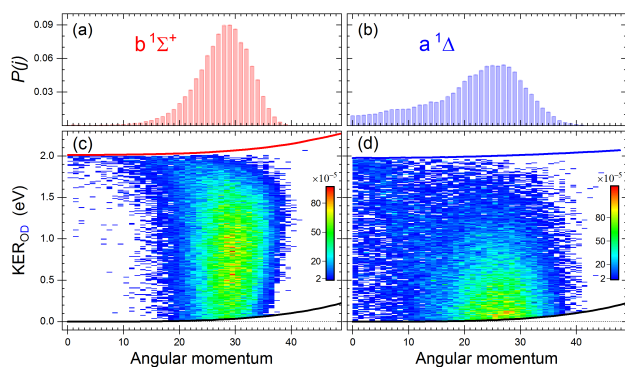


Fig. 3. Normalized angular momentum distribution, $\sum_j P(j) = 1$, of the (a) $b^1\Sigma^+$ and (b) $a^1\Delta$ states of OD^+ populated during D_2O^{2+} fragmentation (see text), as well as the, respective, angular momentum – KER_{OD} correlation maps in panels (c) and (d). The lines in panels (c) and (d) represent the modification of the “appearance window” in Fig. 1(b) for nonzero rotational angular momentum by the addition of a centrifugal potential to both the singlet and triplet potential curves (specifically, $A^3\Pi$ – black, $b^1\Sigma^+$ – red, and $a^1\Delta$ – blue). In the absence of tunneling no dissociating trajectories can appear outside these lines.

events (specifically including the lowest 3P , 1D , and 1S states of oxygen) as a function of $KER_{OD} = p_{OD}^2 / 2\mu_{OD}$ and $\theta_{OD,D}$, where we arbitrarily designate one of the two D^+ fragments “red” — ejected first — a correct “coin flip” assignment for half of the sequential events. Then, we identify the (properly assigned) sequential breakup as the uniform angular stripe marked by the dashed-red rectangular boundary in the figure. Note that the KER distribution of this stripe matches the predicted 0–2.25 eV range (19, 20), indicated by the appearance window in Fig. 1(b) and Fig. 3.

Three observations are appropriate at this point: First, in Fig. 2(c) we show the complete angular distribution of this sequential-fragmentation channel of D_2O^{2+} , which was reconstructed taking advantage of the fact that $N(\theta_{OD,D})$ is nearly uniform (15). In short, identified sequential events within the red boundary in Fig. 2(a) are used to create equivalent events by randomly rotating them to smaller angles until the whole range has a uniform yield within the uncertainty of the data. It is important to note that any other information of each event, like KER_{OD} , is preserved by this reconstruction algorithm (15) (see Ref. (16) for further details).

Second, in Fig. 2(d) we present the $N(KER_{OD}, \theta_{OD,D})$ distribution — a similar distribution to that shown in panel (c) but with the “wrong” fragmentation-step order. In other words, we are plotting sequential breakup occurring via the OD^+ intermediate in the frame assuming a OD^+ intermediate. To generate such a distribution with certainty, we use the events identified as sequential fragmentation via a $D^+ + OD^+$ and shown in Fig. 2(c), but analyze them as if the D^+ was ejected first, i.e. using the reference frames that are not associated with the relevant center-of-mass of each breakup step. In other words, their momenta are calculated in the other Jacobi coordinate arrangement, namely $p_{OD,D}$ and p_{OD} . One can clearly see that the two distributions, shown separately in panels (c) and (d) are significantly different from each other. Both these distributions are also visible in the “raw” data shown in panel (b). Hence, one can associate each D^+ with the relevant fragmentation step. After correctly assigning which D^+ comes from the OD^+ intermediate, we combine the data for all plots

presented below, i.e. we use all sequential events via OD^+ .

Finally, we note that the high degree of rotational excitation in the intermediate OD^+ $b^1\Sigma^+$ and $a^1\Delta$ states, which leads to the sequential breakup signature, has its origin in the strong force towards bond opening on the corresponding 2^1A_1 and $1B_1$ potential surfaces upon the loss of two electrons. In the simplest picture of the electronic structure of water these states are created by the loss of two lone-pair electrons. From simple molecular orbital considerations, losing one or two electrons out of the in-plane $3a_1$ lone pair orbital should lead to an opening of the bond. Streeter *et al.* (17) found that this torque is strong enough to cause the two D^+ fragments, ejected initially near the 104° equilibrium bond angle in a concerted three-body fragmentation on these surfaces, to invert this angle to greater than 180° while they are still close to the oxygen atom. Similar trajectories that lead to the two-body breakup into $D^+ + OD^+$ impart a strong torque on the OD^+ fragment leading to high rotational excitation. Gervais *et al.* (20) also found high rotational excitation in diatomic ion fragments from HOD having insufficient internal energy to predissociate, with the highest being from these two dication states. For the trajectories here that produce the OD^+ ion with enough internal energy to predissociate via the $A^3\Pi$ state, this leads to even higher levels of rotational excitation, peaking near $J = 30$ as shown in Fig. 3. This rotational distribution leaves its signature in the kinetic energies of the atomic fragments after dissociation as discussed below.

Results and Discussion

As we have established above, we can identify and select the events undergoing sequential fragmentation via a $D^+ + OD^+$ intermediate (via OD^+ for short, hereafter) out of all measured $D^+ + D^+ + O$ three-body breakup events. Here, we focus on what one can learn about the sequential process by employing the methodology described in the preceding section.

First, we determine which three-body dissociation limit is associated with sequential fragmentation via OD^+ . To that end, in Fig. 4 we present all the measured $D^+ + D^+ + O + 2e^-$ events (red-solid line), resulting from the absorption of a single 61-eV photon, as a function of the total energy release, i.e. $E_{\text{release}} = KER + E_{e1} + E_{e2}$, where E_{e1} or E_{e2} is the kinetic energy of an electron in the continuum. The expected value of E_{release} for each dissociation limit is evaluated from the known photon energy, the complete dissociation energy of water, and the initial state (i.e. ground state) of the heavy water molecule — those locations are marked by vertical lines and labeled by the oxygen final state in Fig. 4 — though with a small shift down, ~ 0.4 eV, due to experimental uncertainties.* It is evident from the figure that the likelihood of fragmentation to the lowest two dissociation limits, i.e. $O(^3P)$ and $O(^1D)$, is approximately equal, and each of them is more likely than a breakup to the $O(^1S)$ limit. In the same figure we also plot (blue line) the sequential events via OD^+ , selected by $KER_{OD} < 2.3$ eV (see “Native frames analysis” section). Figure 4 clearly shows that the sequential fragmentation via OD^+ leads solely to

*The expected total energy release, E_{release} , is computed by subtracting the complete dissociation energy of the heavy water dication into $D^+ + D^+ + O(^3P)$ from the measured photon energy used in our experiment. The accumulated error in the measured E_{release} and photon energy, as well as uncertainties in the complete dissociation energy of water recommended by NIST, add up to an estimated uncertainty of the order of the energy shift needed to match the measured spectrum shown in Fig. 4 (see supplementary information for further details).

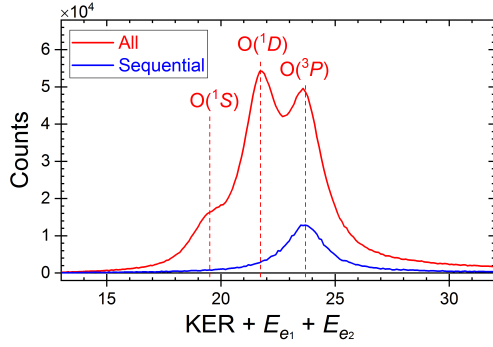


Fig. 4. Total energy release distribution following double photoionization of water, i.e. $N(\text{KER} + E_{e1} + E_{e2})$. The vertical lines indicate the expected energy of each $\text{D}^+ + \text{D}^+ + \text{O}$ dissociation limit, which are labeled by the final state of the oxygen and shifted down by 0.4 eV (see text). Note that sequential fragmentation via OD^+ correlates only with the $\text{D}^+ + \text{D}^+ + \text{O}(^3P)$ dissociation limit.

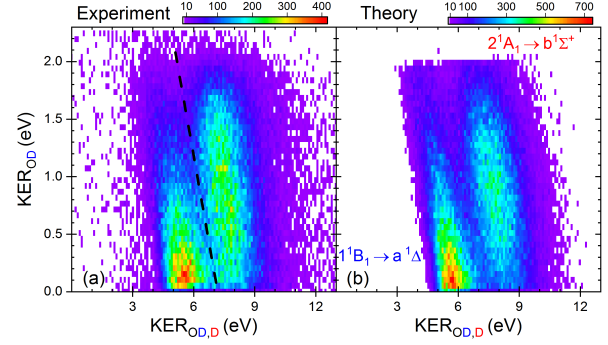


Fig. 5. Sequential fragmentation of D_2O^{2+} into $\text{D}^+ + \text{D}^+ + \text{O}(^3P)$ as a function of $\text{KER}_{\text{OD},\text{D}}$ and KER_{OD} : (a) Experiment and (b) Theory. The two panels nicely match each other, aided by the choice of similar statistics in the theory to match the experimental data quality. The black-dashed line in panel (a) is used to separate the two sequential fragmentation paths (see text), specifically $2^1A_1 \rightarrow b^1\Sigma^+$ (right) from $1^1B_1 \rightarrow a^1\Delta$ (left).

the $\text{D}^+ + \text{D}^+ + \text{O}(^3P)$ dissociation limit[†]. We also note that the electrons associated with this sequential breakup exhibit an energy sharing that is typical for direct double ionization involving no auto-ionization, as shown in Fig. 2(e).

Next, we return to the suggested sequential fragmentation pathway that motivated the choice of water as the subject of this study. As mentioned briefly in the introduction, Streeter *et al.* (17) suggested that the $\text{OD}^+(b^1\Sigma^+)$ is the intermediate state that predissociates, due to spin-orbit coupling with the $A^3\Pi$ state [shown in Fig. 1(b)] (19, 20), into $\text{D}^+ + \text{O}(^3P)$ a few picoseconds after the D_2O^{2+} breaks into $\text{D}^+ + \text{OD}^+(b^1\Sigma^+)$.

Inspection of Fig. 1(a) indicates that the $b^1\Sigma^+$ state of OD^+ correlates to the 2^1A_1 state of D_2O^{2+} . If the latter state is populated by a vertical transition from the D_2O ground state (i.e. removing two electrons without changing the internuclear distances or bond angle, which is a reasonable approximation for ionization by a single photon), then a kinetic energy release of about 7 eV is expected in the first fragmentation step, $\text{D}^+ + \text{OD}^+(b^1\Sigma^+)$, on route to $\text{D}^+ + \text{D}^+ + \text{O}(^3P)$.

To verify this suggested pathway we plot in Fig. 5(a) the measured sequential fragmentation events[‡] leading to $\text{D}^+ + \text{D}^+ + \text{O}(^3P)$ as a function of $\text{KER}_{\text{OD},\text{D}}$ and KER_{OD} , i.e. the KER in the first and second fragmentation step, respectively. One can clearly see the feature centered about the expected $\text{KER}_{\text{OD},\text{D}}$ with a broad, relatively flat, KER_{OD} distribution extending to about 2.1 eV. Thus, affirming the predicted sequential fragmentation path $\text{D}_2\text{O}^{2+}(2^1A_1) \rightarrow \text{D}^+ + \text{OD}^+(b^1\Sigma^+)$ followed by $\text{OD}^+(b^1\Sigma^+) \rightarrow \text{D}^+ + \text{O}(^3P)$.

Unexpected from the speculation in Streeter *et al.* (17), there is a prominent second feature in Fig. 5(a), which is centered about a lower $\text{KER}_{\text{OD},\text{D}}$ of about 5.5 eV. Moreover, the KER_{OD} distribution of this feature peaks near zero and tails off rapidly. The significant differences between the two features suggest another fragmentation pathway.

Examination of the potential energy along the asymmetric stretch coordinate, shown in Fig. 1(a), indicates that the 1^1B_1 state of the dication, at the equilibrium R_{OD} of water

(1.812 a.u.), is about 5.5 eV above the $\text{D}^+ + \text{D}^+ + \text{O}(^3P)$ dissociation limit associated with the first fragmentation step, $\text{D}^+ + \text{OD}^+(a^1\Delta)$. Therefore, we attribute this lower $\text{KER}_{\text{OD},\text{D}}$ feature to sequential fragmentation initiated by double ionization to the 1^1B_1 state, which is consistent with the results of our classical trajectories on the 1^1B_1 potential surface. This state, then, dissociates into $\text{D}^+ + \text{OD}^+(a^1\Delta)$. Later, the $a^1\Delta$ state predissociates into $\text{D}^+ + \text{O}(^3P)$ due to its spin-orbit coupling with $A^3\Pi$ state of OD^+ . We are not aware of a reported lifetime for the $a^1\Delta$ state, however we expect it to be similar to that of the $b^1\Sigma^+$ state given that both are coupled to the $A^3\Pi$ state, and their spin-orbit matrix elements have similar magnitudes according to calculations by de Vivie *et al.* (19). In summary, we discovered another sequential fragmentation path, namely $\text{D}_2\text{O}^{2+}(1^1B_1) \rightarrow \text{D}^+ + \text{OD}^+(a^1\Delta)$ followed by $\text{OD}^+(a^1\Delta) \rightarrow \text{D}^+ + \text{O}(^3P)$.

In Fig. 5 we also compare the measured and simulated KER-correlation maps to each other. In this simulation we assumed that the cross sections for double ionization are the same for the 2^1A_1 and 1^1B_1 states. Both features in the figure match very well, suggesting that our classical trajectory approach, though it approximates the nonadiabatic dynamics, captures the essence of the physical process. Moreover, the measured KER-correlation map enables separation between the two sequential-fragmentation pathways, thus allowing their direct comparison without recourse to theory. This separation[§] is accomplished by selecting events to the right ($2^1A_1 \rightarrow b^1\Sigma^+$) or left ($1^1B_1 \rightarrow a^1\Delta$) of the black-dashed line shown in Fig. 5(a). Note that this line has a slight tilt that reflects a constant total KER (specifically, we used 7.18 eV in the analysis).

In Fig. 6 we compare the measured KER distributions to the calculated ones for both steps of each sequential fragmentation path. As neither our theory nor experiment are absolute, we scale them to match using a least square fit. Specifically, we scale the theory to preserve the measured information on the relative likelihood of the two sequential fragmentation paths. Note that the calculated KER distribution associated with the

[†]The broad energy distribution (clearly visible in the sequential breakup) is mainly due to the extended target along the light-propagation direction, energy resolution, and the spread in center-of-mass momentum that cannot be corrected for because the neutral oxygen fragment is not detected, but evaluated from momentum conservation.

[‡]We use the same conditions to select the D_2O^{2+} sequential fragmentation events, specifically $\text{KER}_{\text{OD}} < 2.3$ eV (see “Native frames analysis” section for details).

[§]This visualization of our pathway separation method, though correct, is simplified in practice by plotting the same data as a function of $\text{KER}_{\text{OD},\text{D}} + \text{KER}_{\text{OD}}$ and $\text{KER}_{\text{OD},\text{D}} - \text{KER}_{\text{OD}}$, i.e. a 45° rotation of the spectrum in Fig. 5. Then, we project it onto the $\text{KER}_{\text{total}} = \text{KER}_{\text{OD},\text{D}} + \text{KER}_{\text{OD}}$ axis, and separate events larger than $\text{KER}_{\text{total}} = 7.18$ eV to one channel ($b^1\Sigma^+$) while events with smaller $\text{KER}_{\text{total}}$ are associated with the other channel ($a^1\Delta$).

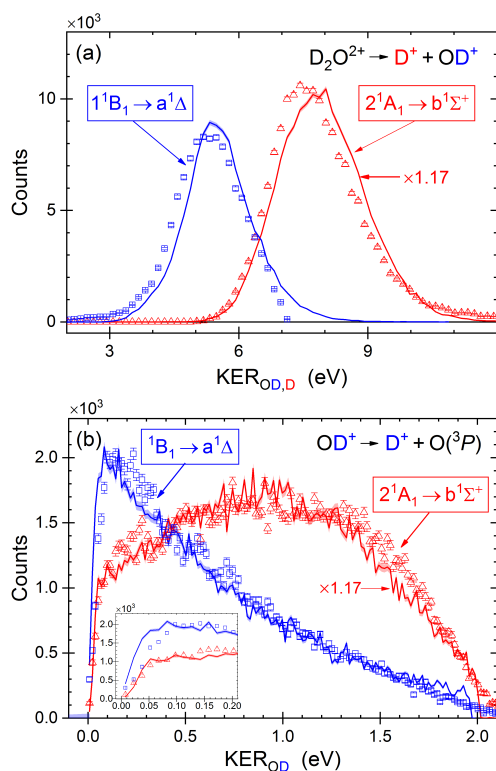


Fig. 6. Sequential fragmentation of D_2O^{2+} into $D^+ + D^+ + O(^3P)$ as a function of (a) $KER_{OD,D}$ and (b) KER_{OD} (Inset: Zoom-in of low energy range). Comparison of experiment (symbols) and normalized theory (solid lines) for the two fragmentation pathways (and associated states) identified and separated using Fig. 5(a) (see text). As indicated on the figure, the theory scaling of one path is a factor of 1.17 larger than the other one (see text). The high energy cutoff in the measured 1^1B_1 to $a^1\Delta$ data in the upper panel is likely due to the imperfect separation of the two channels by the black-dashed line in Fig. 5.

$2^1A_1 \rightarrow b^1\Sigma^+$ path is scaled by an additional factor of 1.17 relative to the scaling of the $1^1B_1 \rightarrow a^1\Delta$ path, as indicated in Fig. 6. This difference is mainly due to the relative magnitude of the cross sections for double photoionization by a single 61-eV photon landing on the 2^1A_1 and 1^1B_1 states of D_2O^{2+} .

Our classical trajectory calculations propagate the same number of trajectories (10^6) on each dication surface, with no regard to the cross section for producing that dication state in double photoionization. As a result those calculations can accurately reflect the branching ratios between two- and three-body breakup channels on each electronic state, but provide no information about the photoionization cross sections. In contrast, the experiment does determine the ratio between the two, thus providing a test of the magnitudes of the cross sections to be determined by future double photoionization calculations.

At a glance, the calculated and measured KER distributions associated with the $D_2O^{2+} \rightarrow D^+ + OD^+$ breakup, shown in Fig. 6(a), match each other nicely. However, a careful inspection shows that the calculated distributions are shifted up by about 0.15 eV. We suspect that this difference stems from approximating the initial wave function of D_2O , which is projected to the D_2O^{2+} states, by a product of normal mode harmonic oscillators instead of a more accurate representation including the effects of the anharmonicity in the ground state potential energy surface. Similar discrepancies have been ob-

served in H_2 and were corrected by using a Morse potential to represent the initial state (25).

The calculated and measured KER distribution associated with the second fragmentation step, namely $OD^+ \rightarrow D^+ + O$ shown in Fig. 6(b), match very well for both sequential fragmentation paths. The differences between the KER distributions associated with these two fragmentation paths, noticeable in Fig. 5, become more apparent. The sequential fragmentation via the $b^1\Sigma^+$ state yields a broad, relatively flat, KER distribution peaked around 0.9 eV, while the fragmentation via the $a^1\Delta$ state peaks at much lower KER, ~ 0.15 eV, and falls off rapidly with increasing KER.

It is important to note that the KER in the predissociation of the OD^+ images the internal energy of this diatomic ion above the $O(^3P)$ dissociation limit, i.e. the internal energy stored in highly excited vibrational and rotational states. This assertion is correct if the assumption, used in our modeling, that all rovibrational states above the $D^+ + O(^3P)$ dissociation limit predissociate, is valid. The comparison of experiment and theory in Fig. 6(b) validates that assumption. The remaining population, in the lower rovibrational states of the $a^1\Delta$ and $b^1\Sigma^+$ states of OD^+ , is measured as the dominant two-body breakup, $D^+ + OD^+$ [see previous reports on H_2O (17, 18)].

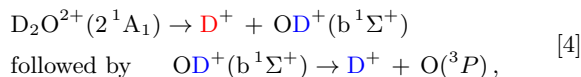
In addition to the internal energy of the OD^+ ion, our classical trajectory simulations provide the angular momentum distribution, $P(J)$, of each state of OD^+ shown in Fig. 3. Similar to the KER distributions, here too, the $P(J)$ distributions of the $a^1\Delta$ and $b^1\Sigma^+$ states are different. The former peaks at a lower J (~ 26) and has a long tail extending all the way to $J = 0$, while the latter peaks around $J = 30$ and is much narrower.

There are two observable consequences of these predicted J distributions. First, the high rotational angular momentum implies that the orientation of the long-lived OD^+ fragment will not be correlated with the direction of emission of the first D^+ fragment. This is in agreement with the nearly uniform $\theta_{OD,D}$ angular distribution seen in the experiment in Fig. 2. Second, the high rotational angular momentum of the OD^+ fragment results in a barrier with respect to the dissociation limit (i.e., centrifugal barrier) indicated in Fig. 3(c,d). The internal energy of the OD^+ fragment is reflected in the distribution of KER_{OD} to which all angular momenta contribute. The threshold behavior in Fig. 6(b) in which the KER distribution vanishes as KER_{OD} goes to zero has its origin in the fact that only a small fraction of the OD^+ ions is produced with zero rotational angular momentum, and only this contribution can yield zero KER. This threshold behavior of the KER_{OD} distribution in the trajectory calculations is also seen in the experimental data in close agreement with the theoretical prediction.

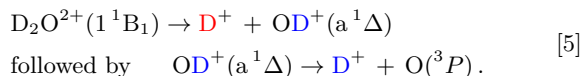
Summary and Outlook

We studied the sequential fragmentation of water following double ionization by a single photon in unprecedented detail. The events associated with this process were separated experimentally from other fragmentation processes leading to the same final three-body channel, namely $D^+ + D^+ + O(^3P)$, using the native frames method and taking advantage of the rotation of the metastable OD^+ intermediate in the fragmentation plane. We identified two sequential-fragmentation pathways involving different electronic states and followed them step by

step. Specifically the routes are:



and



In both pathways, the second fragmentation step involves predissociation of the OD^+ due to spin-orbit coupling of the populated $\text{b}^1\Sigma^+$ and $\text{a}^1\Delta$ states with the $\text{A}^3\Pi$ state.

The results of our classical trajectory propagation on the D_2O^{2+} potential surfaces are overall in excellent agreement with the experimental data associated with both sequential fragmentation paths and the steps each one undergoes, which are detailed in Eqs. 4 and 5. We draw particular attention to our ability to calculate the internal energy of the intermediate OD^+ molecule, and probe it experimentally above the $\text{D}^+ + \text{O}(^3\text{P})$ dissociation limit. Likewise, the angular momentum distribution of the intermediate OD^+ molecule has been computed and the predicted impact on the low KER distribution has been measured.

Though our methodology has been demonstrated for sequential fragmentation of water following double ionization by a single photon, it is not limited to this specific case. The combination of kinematically complete momentum imaging measurements, classical trajectory simulations on the relevant potential energy surface, and the native frames method should be applicable to a wide range of polyatomic molecules as long as the energy deposited in the system is known and there is a clear signature enabling identification of sequential fragmentation from other processes, like the rotation of the intermediate molecular fragment in our test case. This methodology enhances our capabilities for exploring molecular reaction dynamics on the potential energy surface around asymmetric stretch that is commonly the path for forming an intermediate molecular fragment in route to sequential fragmentation. The observation of sequential steps in a molecular dissociation reaction via their unambiguous signature in the momenta of the fragments has added the dimension of time to an essentially time-independent measurement.

Data Archival. The data that support the findings of this study are available from the corresponding author upon reasonable request.

ACKNOWLEDGMENTS. We thank the staff at the Advanced Light Source for operating the beamline and providing the photon beam. Work at LBNL was performed under the auspices of the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division under Contract No. DEAC02-05CH11231, using the Advanced Light Source (ALS), the National Energy Research Computing Center (NERSC), a DOE Office of Science User Facility, and the Lawrence computational cluster resource provided by the IT Division at the LBNL. JRML personnel were supported by Grant No. DE-FG02-86ER13491 from the same funding agency. UNR personnel were supported by a National Science Foundation (NSF) grant No. 1807017. R.D. and D.T. acknowledge support from Deutsche Forschungsgemeinschaft via Sonderforschungsbereich 1319 (ELCH). A.G. was supported by the ALS through a Doctoral Fellowship in Residence.

- J. P. Marangos. The measurement of ultrafast electronic and structural dynamics with x-rays. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 377(2145):20170481, 2019. This article is part of the theme issue, Measurement of ultrafast electronic and structural dynamics with X-rays.
- Romain Geneaux, Hugo J. B. Marroux, Alexander Guggenmos, Daniel M. Neumark, and Stephen R. Leone. Transient absorption spectroscopy using high harmonic generation: a review of ultrafast x-ray dynamics in molecules and solids. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 377(2145):20170463, 2019.
- Matthew R. Ware, James M. Glowia, Adi Natan, James P. Cryan, and Philip H. Bucksbaum. On the limits of observing motion in time-resolved x-ray scattering. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 377(2145):20170477, 2019.
- J. Ullrich, R. Moshhammer, R. Dörner, O. Jagutzki, V. Mergel, H. Schmidt-Böcking, and L. Spielberger. Recoil-ion momentum spectroscopy. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 30(13):2917, 1997.
- R. Dörner, V. Mergel, O. Jagutzki, L. Spielberger, J. Ullrich, R. Moshhammer, and H. Schmidt-Böcking. Cold target recoil ion momentum spectroscopy: a 'momentum microscope' to view atomic collision dynamics. *Physics Reports*, 330:95, 2000.
- J. Ullrich, R. Moshhammer, A. Dorn, R. Dörner, L. Ph H Schmidt, and H. Schmidt-Böcking. Recoil-ion and electron momentum spectroscopy: reaction-microscopes. *Reports on Progress in Physics*, 66(9):1463, 2003.
- Akiyoshi Hishikawa, Hirokazu Hasegawa, and Kaoru Yamanouchi. Sequential three-body Coulomb explosion of CS_2 in intense laser fields appearing in momentum correlation map. *Chemical Physics Letters*, 361:245–250, 2002.
- John D. Savee, Vadim A. Mozhayskiy, Jennifer E. Mann, Anna I. Krylov, and Robert E. Continetti. The role of excited-state topology in three-body dissociation of sym-triazine. *Science*, 321(5890):826–830, 2008.
- N. Neumann, D. Hant, L. Ph. H. Schmidt, J. Titze, T. Jahnke, A. Czaasch, M. S. Schöffler, K. Kreidl, O. Jagutzki, H. Schmidt-Böcking, and R. Dörner. Fragmentation dynamics of CO_2^{3+} investigated by multiple electron capture in collisions with slow highly charged ions. *Phys. Rev. Lett.*, 104:103201, 2010.
- Cong Wu, Chengyin Wu, Di Song, Hongmei Su, Yudong Yang, Zhifeng Wu, Xianrong Liu, Hong Liu, Min Li, Yongkai Deng, Yunquan Liu, Liang-You Peng, Hongbing Jiang, and Qihuang Gong. Nonsequential and sequential fragmentation of CO_2^{3+} in intense laser fields. *Phys. Rev. Lett.*, 110:103601, 2013.
- Benji Wales, Eric Bisson, Reza Karimi, Samuel Beaulieu, Ali Ramadhan, Mathieu Giguère, Zijian Long, Wing-Ki Liu, Jean-Claude Kieffer, François Légaré, and Joseph Sanderson. Coulomb imaging of the concerted and stepwise break up processes of OCS ions in intense femtosecond laser radiation. *J. Elect. Spectr. Rel. Phenom.*, 195:332, 2014.
- R. Guillemin, P. Decleva, M. Stener, C. Bomme, T. Marin, L. Journel, T. Marchenko, R.K. Kushawaha, K. Jänkälä, N. Trcera, K.P. Bowen, D.W. Lindle, M.N. Piancastelli, and M. Simon. Selecting core-hole localization or delocalization in CS_2 by photofragmentation dynamics. *Nat. Comm.*, 6:6166, 2015.
- Utug Ablikim, Cédric Bomme, Evgeny Savelyev, Hui Xiong, Rajesh Kushawaha, Rebecca Boll, Kasra Amini, Timur Osipov, David Kilcoyne, Artem Rudenko, Nora Berrah, and Daniel Rolles. Isomer-dependent fragmentation dynamics of inner-shell photoionized difluoriodobenzene. *Phys. Chem. Chem. Phys.*, 19:13419–13431, 2017.
- Xiaoyan Ding, M. Haertelt, S. Schlauderer, M. S. Schuurman, A. Yu. Naumov, D. M. Vilenueve, A. R. W. McKellar, P. B. Corkum, and A. Staudte. Ultrafast dissociation of metastable CO^{2+} in a dimer. *Phys. Rev. Lett.*, 118:153001, 2017.
- Jyoti Rajput, T. Severt, Ben Berry, Bethany Jochim, Peyman Feizollah, Balram Kaderiya, M. Zohrabi, U. Ablikim, Farzaneh Ziaee, Kanaka Raju P., D. Rolles, A. Rudenko, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak. Native frames: Disentangling sequential from concerted three-body fragmentation. *Phys. Rev. Lett.*, 120(10):103001, 2018.
- T. Severt, Jyoti Rajput, Ben Berry, Bethany Jochim, Peyman Feizollah, Balram Kaderiya, M. Zohrabi, U. Ablikim, Farzaneh Ziaee, Kanaka Raju P., D. Rolles, A. Rudenko, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak. Native frames: A new approach for separating sequential and concerted three-body fragmentation. *Phys. Rev. A*. In preparation.
- Zachary L. Streeter, Frank L. Yip, Robert R. Lucchese, Benoit Gervais, Thomas N. Rescigno, and C. William McCurdy. Dissociation dynamics of the water dication following one-photon double ionization. I. Theory. *Phys. Rev. A*, 98:053429, 2018.
- D. Reedy, J. B. Williams, B. Gaire, A. Gatton, M. Weller, A. Menssen, T. Bauer, K. Henrichs, Ph. Burzynski, B. Berry, Z. L. Streeter, J. Sartor, I. Ben-Itzhak, T. Jahnke, R. Dörner, Th. Weber, and A. L. Landers. Dissociation dynamics of the water dication following one-photon double ionization. II. Experiment. *Phys. Rev. A*, 98:053430, 2018.
- Regina de Vivie, Christel M. Marian, and Sigrid D. Peyerimhoff. Spin-forbidden transitions in the presence of an intersystem crossing: Application to the $\text{b}^1\Sigma^+$ state in OH^+ . *Chemical Physics*, 112(3):349–361, 1987.
- B. Gervais, E. Giglio, L. Adoui, A. Cassimi, D. Duflet, and M. E. Galassi. The H_2O^{2+} potential energy surfaces dissociating into H^+/OH^+ : Theoretical analysis of the isotopic effect. *The Journal of Chemical Physics*, 131(2):024302, 2009.
- Hans-Joachim Werner, Peter J. Knowles, Gerald Knizia, Frederick R. Manby, and Martin Schütz. Molpro: a general-purpose quantum chemistry program package. *WIREs Computational Molecular Science*, 2(2):242–253, 2012.
- H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, et al. Molpro, version 2015.1, a package of *ab initio* programs, 2015, 2012. see <http://www.molpro.net>.
- Kirk A. Larsen, Thomas N. Rescigno, Travis Severt, Zachary L. Streeter, Wael Iskandar, Saijocha Heck, Averell Gatton, Elio G. Champenois, Richard Strom, Bethany Jochim, Dylan Reedy, Demitri Call, Robert Moshhammer, Reinhard Dörner, Allen L. Landers, Joshua B. Williams, C. William McCurdy, Robert R. Lucchese, Itzik Ben-Itzhak, Daniel S. Slaughter, and Thorsten Weber. Photoelectron and fragmentation dynamics of the $\text{H}^+ + \text{H}^+$ dissociative channel in NH_3 following direct single-photon double ionization. *Phys. Rev. Research*, 2:043056, 2020.

- 613 24. Zhenjie Shen, Enliang Wang, Maomao Gong, Xu Shan, and Xiangjun Chen. Fragmenta-
614 tion dynamics of carbonyl sulfide in collision with 500 ev electron. *The Journal of Chemical*
615 *Physics*, 145(23):234303, 2016.
- 616 25. T. Weber, A. O. Czasch, O. Jagutzki, A. K. Müller, V. Mergel, A. Kheifets, E. Roten-
617 berg, G. Meigs, M. H. Prior, S. Daveau, A. Landers, C. L. Cocke, T. Osipov, R. Díez
618 Muiño, H. Schmidt-Böcking, and R. Dörner. Complete photo-fragmentation of the deuterium
619 molecule. *Nature*, 431:437, 2004.

DRAFT

3.4 Native frames method tutorial

Below we present a draft that follows the publication presenting the native frames method included in Section 3.2. This follow-up draft further elaborates on the previous paper, effectively providing a tutorial for researchers planning to implement our analysis. The manuscript presents the same measurement on the strong-field dissociative ionization of OCS into $O^+ + C^+ + S^+$ as an example, but in further detail compared to the paper in Section 3.2. In addition, we include discussion about the implications of using a polar angle to identify sequential fragmentation and how contributions outside of the fragmentation plane can affect the angular distribution. We also further describe the utility of the Euler angles and use them to determine that an SO^{2+} intermediate is not formed. Finally, we give some specific examples indicating where separating sequential from concerted fragmentation may be beneficial. Although the paper has not been published yet, it has already helped others within the James R. Macdonald Laboratory successfully implement the native frames method [133].

In this paper, I worked in collaboration with our former post-doc, Jyoti Rajput, as well as the research groups of Artem Rudenko, Daniel Rolles, and Brett Esry. Specifically, Artem’s and Daniel’s groups mainly contributed to the data collection while Brett Esry contributed to the analysis and exploring the implications of using a polar angle to identify sequential breakup. I performed the analysis and wrote the final manuscript with the help of all coauthors.

Native frames: A new approach for separating sequential and concerted three-body fragmentation

T. Severt, Jyoti Rajput,* Ben Berry, Bethany Jochim, Peyman Feizollah, Balram Kaderiya, M. Zohrabi, U. Ablikim, Farzaneh Ziaee, Kanaka Raju P., D. Rolles, A. Rudenko, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak†

*J. R. Macdonald Laboratory, Physics Department,
Kansas State University, Manhattan, Kansas 66506*

(Dated: June 9, 2021)

Disentangling sequential and concerted three-body fragmentation has been a long-standing endeavor in studies of molecular dynamics. To accomplish this goal, we recently introduced a novel method to separate sequential from concerted breakup, where the sequential events are analyzed in their native frames [J. Rajput *et al.*, Phys. Rev. Lett. **120**, 103001 (2018)]. The essence of this method is the use of the Jacobi coordinates’ conjugate momenta to reduce the dimensionality of the multi-body fragmentation in combination with a clear signature for sequential breakup. To demonstrate this method, we employ coincidence momentum imaging to study the strong-field dissociative ionization of OCS into $O^+ + C^+ + S^+$, which typically undergoes concerted fragmentation or sequential breakup involving either a metastable CO^{2+} or CS^{2+} molecule. We identify sequential breakup using a uniform distribution as a function of the angle between the conjugate momenta, associated with the first and second fragmentation steps, which is due to the rotation of the intermediate molecule in the fragmentation plane. By exploiting this uniform distribution, we separate the sequential and concerted distributions in any plot created from the measured momenta.

I. INTRODUCTION

When a molecule or cluster is ionized, the propagation of the dissociating wavepacket on the potential energy landscape determines the dynamics leading to fragmentation. Many experimental techniques image the asymptotic momentum distributions of the resulting fragments to learn about the evolution of the system following ionization. Due to the complexity of even the simplest of molecules, extracting information about the fragmentation dynamics is challenging and is a longstanding goal of the molecular dynamics community, e.g., see [1–24].

On occasion, researchers try to identify specific dynamical processes using signatures found in the final momentum distributions. One such example is the sequential fragmentation of polyatomic molecules, where two or more chemical bonds break in a stepwise fashion. Between the fragmentation steps, the intermediate metastable molecule may rotate, providing a signature to distinguish sequential from concerted breakup, in which all bonds break quickly relative to the rotational period of the molecule [25].

For example, separating concerted from sequential breakup distributions is vital for interpreting many experiments, especially when invoking the axial-recoil approximation [26]. One relevant example is the transformation of the recoil-frame photoelectron angular distributions (RFPADs) to the molecular-frame photoelectron angular distributions (MFPADs) [14, 17, 27–29] for data containing sequential fragmentation [30]. If the intermediate molecule (hereafter referred to as “intermediate” in

short) rotates for some time after ionization, the intermediate’s asymptotic heavy-particle momenta no longer determine the initial orientation of the molecule at the time of ionization. However, the momentum of the first ejected heavy fragment may relate to the initial orientation. Therefore, choosing the fragment not involved in the rotation as a reference to define the RFPAD [30] allows for a more meaningful interpretation of the RFPAD distribution. Furthermore, to obtain meaningful MFPAD distributions, it is vital to first eliminate any sequential fragmentation contributions.

Since sequential breakup results in the breakdown of the axial-recoil approximation, it poses additional difficulties when interpreting photofragmentation angular distributions relative to the polarization of the light [31, 32], relative angular distributions between fragments [33–35], and more. These examples show the need for a technique that allows not only the identification of sequential fragmentation but also its separation and subtraction from other competing processes, leading to separate sequential- and concerted-breakup plots. It is worth noting, however, that events contained in the remaining concerted fragmentation distribution do not necessarily satisfy the axial recoil approximation. In some instances, researchers have shown that the final momentum distributions of concerted breakup can be dramatically different than what is naively expected based on the initial geometry of the molecule [36, 37].

For the past few decades, researchers have used a variety of strategies to distinguish sequential from concerted three-body fragmentation in molecular breakup [18, 25, 30, 33, 38–63]. Furthermore, identifying three-body sequential breakup finds applications in other fields, including the study of the decay of mesons [64–66] and nuclear fragmentation [67–72]. A specific nuclear fragmentation example is the decay of the Hoyle state [67–71], where

* Permanent address: Department of Physics and Astrophysics, University of Delhi, Delhi 110007, INDIA.

† ibi@phys.ksu.edu

^{12}C predominantly decays sequentially into three α particles via an intermediate $^8\text{Be}^*$.

To distinguish sequential from concerted breakup, the coincident three-dimensional momentum imaging of the resulting breakup is typically crucial. Of the many plotting strategies developed to recognize sequential fragmentation [18, 30, 33, 41–62], Dalitz plots and Newton diagrams became the gold standards for identifying and even partially separating sequential from concerted breakup [18, 30, 41, 47–62].

Improving on Dalitz plots and Newton diagrams, we recently demonstrated a novel analysis method enabling the separation of sequential and concerted breakup by studying three-body sequential fragmentation in the “native frame” of each step [63]. By plotting the distribution of angles between the conjugate momenta of the Jacobi coordinates [73–77], sequential fragmentation is identified as a uniform angular distribution due to the rotation of the intermediate molecule in the fragmentation plane, which is defined by the measured momenta of the fragments. Furthermore, we can reconstruct the parts of the sequential fragmentation distribution masked by concerted and other sequential-breakup processes by exploiting this uniform angular distribution. Finally, we separate the concerted fragmentation distributions by subtracting all possible sequential breakup contributions from the complete data set [63].

In this paper, we describe the native-frames method introduced in Ref. [63] in greater detail and highlight the wide variety of information revealed by such analysis, using the dissociative triple ionization of OCS as an example. In particular, we study the fragmentation of OCS into $\text{O}^+ + \text{C}^+ + \text{S}^+$, which undergoes two possible sequential pathways involving either a CO^{2+} or CS^{2+} intermediate metastable molecule [52, 58, 59]. The native-frames method is not unique to OCS and applies to many systems, not only molecules that undergo sequential three-body fragmentation. The generality of the native frames analysis approach stems from the use of the Jacobi coordinates’ conjugate momenta to reduce the dimensionality of the data and analyze it systematically, as well as provide a framework to generalize toward fragmentation processes involving more than three fragments.

II. EXPERIMENTAL METHOD

In our experiment, an ultrafast and intense laser field initiates the triple ionization and dissociation of OCS molecules. Briefly, we produce the laser pulse using an ultrafast Ti:Sapphire chirped-pulse-amplification laser system (KMLabs) with a 10-kHz repetition rate, maximum pulse energy of 2 mJ, central wavelength of 790 nm, and a pulse duration of 23 fs (full-width-half-maximum in intensity).

About 180 μJ of the laser beam is focused onto a supersonic jet using a spherical mirror ($f = 7.5\text{ cm}$), producing a peak intensity of $(5.6 \pm 0.8) \times 10^{14}\text{ W/cm}^2$. The peak in-

tensity is determined by measuring the recoil momentum distributions of Ne^+ ions along the laser polarization. Then, we identify the “kink” in the kinetic energy distribution associated with twice the pondermotive energy, which indicates the transition where rescattered electrons become dominant over the direct electrons [78].

We employ the cold-target-recoil-ion-momentum-spectroscopy (COLTRIMS) technique [6, 8] to measure all charged atomic and molecular products of OCS in coincidence, using a time- and position-sensitive detector, allowing us to compute the three-dimensional momentum distributions. To limit the total count rate on the detector and further cool the OCS molecules in the supersonic jet, we add a He buffer gas at a partial-pressure ratio of 99 to 1 (He to OCS).

The main channel of interest in this work is the three-body breakup of OCS into $\text{O}^+ + \text{C}^+ + \text{S}^+$. In addition, we analyze the two-body $\text{CO}^{2+} + \text{S}^+$ and $\text{CS}^{2+} + \text{O}^+$ fragmentation channels. These channels are effectively a subset of sequential fragmentation events where the metastable intermediate dications, CO^{2+} or CS^{2+} , do not dissociate before striking the detector — i.e., the metastable state’s lifetime is longer than its few microsecond time-of-flight (TOF) to the detector. It is important to note that we analyze all fragmentation channels included in this paper in the center-of-mass (CM) frame of reference of the recoiling OCS^{3+} molecule.

III. IDENTIFYING SEQUENTIAL FRAGMENTATION

To determine if three-body sequential fragmentation occurs, previous studies identified its signatures in Newton diagrams and Dalitz plots [18, 30, 41, 47–62]. In Fig. 1, we show an example Newton diagram and Dalitz plot for the three-body fragmentation of OCS into $\text{O}^+ + \text{C}^+ + \text{S}^+$ with marked features associated with sequential breakup involving the intermediate CO^{2+} and CS^{2+} molecules.

In the case of the Newton diagram, which is a momentum correlation map of the three fragments, the signature of sequential fragmentation is a circular feature, which is attributed to the rotation of the intermediate molecule in the fragmentation plane [47]. For OCS fragmentation, when plotting the Newton diagram with the S^+ momentum fixed to the x axis, as shown in Fig. 1(a), sequential breakup involving the CO^{2+} intermediate emerges as off-set semicircles. On the other hand, sequential fragmentation involving the CS^{2+} intermediate is a “sprinkler”-like feature, as indicated by the dotted line determined from the distribution of this sequential channel after separation from competing channels, as described in Section VIB. To make sequential breakup involving the CS^{2+} intermediate appear as a circular feature, one must create a Newton plot with the O^+ momentum fixed to the x axis instead.

The Dalitz plot [64], which displays the energy sharing

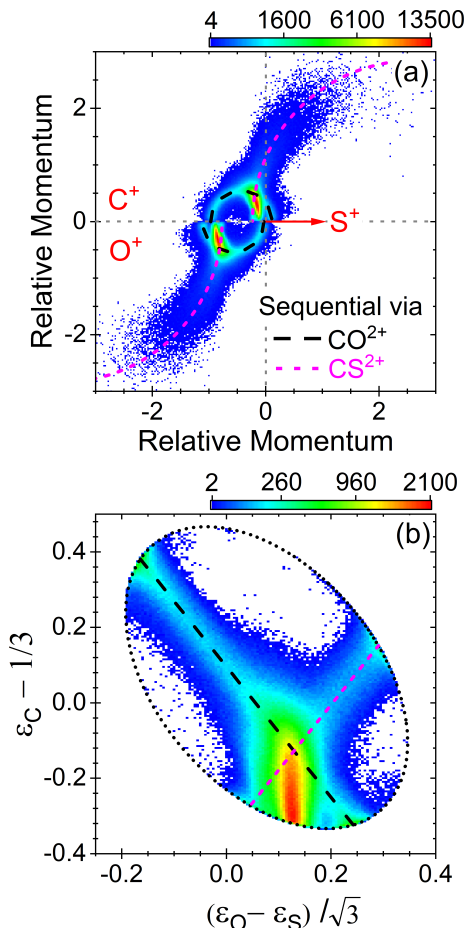


FIG. 1. (Color online) (a) Newton diagram for the three-body fragmentation of OCS into $O^+ + C^+ + S^+$. The momentum of the S^+ fragment is chosen to be along the x axis. The C^+ and O^+ momenta are divided by $|\mathbf{P}_S|$ and placed in the upper and lower halves of the plot, respectively. The black dashed offset semicircles represent the sequential fragmentation process via the CO^{2+} intermediate. The magenta dashed lines represent the sequential fragmentation process via the CS^{2+} intermediate determined from our analysis presented in Section VI B. (b) The Dalitz plot with straight black and magenta dashed lines representing the expected energy relation for sequential fragmentation via the CO^{2+} and CS^{2+} intermediate molecules, respectively. Specifically, ε_i represents the scaled energy of fragment i , that is the kinetic energy of that fragment divided by the total kinetic energy released by all the measured atomic fragments. The black dotted oval represents the boundaries determined by momentum conservation.

among the fragments, is another plotting method used to identify sequential fragmentation. The typical signature of sequential breakup, including in our case, is a distribution following a straight line that spans the range allowed by momentum conservation, as shown for three-body OCS fragmentation in Fig. 1(b). The distributions appear as straight lines due to the rotation of the intermediate molecule in the fragmentation plane and energy conservation, which forces the kinetic energies of each

fragment of the intermediate molecule, in the CM of the parent molecular ion, to depend on the final breakup angle relative to the first step. In other words, the kinetic energy of a fragment is larger or smaller if it breaks in the same or opposite direction of the intermediate molecule's CM momentum, respectively. Additionally, the energy of each fragment changes as a function of the breakup angle, filling in the distribution along the line. The Dalitz plot has been used to separate a subset of the sequential breakup from the concerted fragmentation events to learn more about the steps of the sequential breakup [54, 56] and address the enhancement or suppression of sequential fragmentation rates under different experimental conditions [58].

Since three-body sequential fragmentation occurs in two steps, it is natural to study it in the native frames of reference associated with the first and second breakup steps [63]. In this section, we derive the conjugate momenta of the Jacobi coordinates, which are the natural coordinates describing the native frames of reference and have long been used to study few-body systems [73–77]. Furthermore, we show that identifying sequential fragmentation processes using the native-frames method reduces to choosing one of the several possible Jacobi sets, specifically demonstrated on OCS as an example.

A. Defining the native frames of reference

The native frames allows one to reduce the dimensionality of the multi-body fragmentation process observed by using the Jacobi coordinates [73–77] and their conjugate momenta to analyze momentum imaging data. The benefits of the simplification of the data, by reducing the number of dimensions, is widely applicable and can be naturally extended to a larger number of fragments. We guide one through the application of this method in detail using three-body fragmentation of OCS^{3+} as an example.

Consider the sequential three-body fragmentation of an arbitrary ABC molecule, where the two breakup steps are given by

$$\begin{aligned} ABC &\rightarrow AB + C & (1^{\text{st}} \text{ step}), \\ AB &\rightarrow A + B & (2^{\text{nd}} \text{ step}), \end{aligned}$$

and the three-dimensional momenta of all fragments are measured in coincidence [79]. In the first step, the energy deposited into the system leads to the breakup of the ABC molecule into $AB + C$, where the AB molecule is in a distribution of rovibrational states, some of which are metastable with a corresponding lifetime. In the second step, these metastable states dissociate into $A + B$ after rotating for some time that typically exceeds their lifetime.

To analyze sequential breakup, we begin with the Jacobi coordinates [73–77], shown schematically in

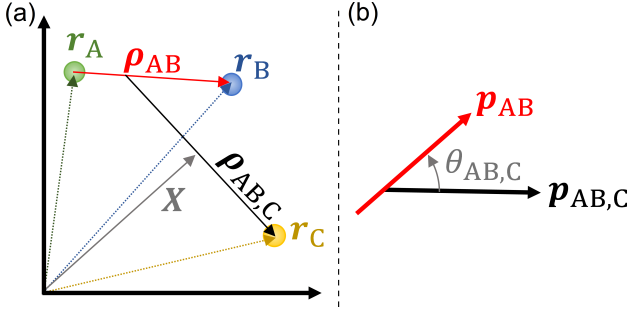


FIG. 2. (Color online) (a) Definition of the Jacobi coordinates, $\boldsymbol{\rho}_{AB,C}$ and $\boldsymbol{\rho}_{AB}$, as well as the CM position vector $\mathbf{X}$, for an arbitrary ABC molecule in some laboratory-fixed frame [73–77]. (b) The definition of the angle $\theta_{AB,C}$ between the relative momenta, $\mathbf{p}_{AB}$ and $\mathbf{p}_{AB,C}$ (see text).

Fig. 2(a). These coordinates are

$$\boldsymbol{\rho}_{AB,C} = \mathbf{r}_C - \frac{1}{m_{AB}} (m_A \mathbf{r}_A + m_B \mathbf{r}_B), \quad (1)$$

$$\boldsymbol{\rho}_{AB} = \mathbf{r}_B - \mathbf{r}_A, \quad (2)$$

where $\boldsymbol{\rho}_{AB,C}$ and $\boldsymbol{\rho}_{AB}$ represent the relative position vectors. Note that the comma, in this notation, separates between the molecular fragments moving apart. The position of the CM of the ABC molecule is

$$\mathbf{X} = \frac{1}{M} (m_A \mathbf{r}_A + m_B \mathbf{r}_B + m_C \mathbf{r}_C). \quad (3)$$

The total mass of the intermediate AB molecule is

$$m_{AB} = m_A + m_B, \quad (4)$$

and the total mass of the parent ABC molecule is

$$M = m_{AB} + m_C. \quad (5)$$

From Eq. (1), the conjugate momentum of $\boldsymbol{\rho}_{AB,C}$ is

$$\mathbf{p}_{AB,C} = \mu_{AB,C} \dot{\boldsymbol{\rho}}_{AB,C} = \frac{m_{AB}}{M} \mathbf{P}_C - \frac{m_C}{M} (\mathbf{P}_A + \mathbf{P}_B), \quad (6)$$

where $\mathbf{P}_A$, $\mathbf{P}_B$, and $\mathbf{P}_C$ are the lab-frame momenta (more precisely, the fragments' momenta in the ABC CM frame) and the reduced mass associated with $\boldsymbol{\rho}_{AB,C}$ is

$$\frac{1}{\mu_{AB,C}} = \frac{1}{m_{AB}} + \frac{1}{m_C}. \quad (7)$$

Similarly, the conjugate momentum of $\boldsymbol{\rho}_{AB}$ is

$$\mathbf{p}_{AB} = \mu_{AB} \dot{\boldsymbol{\rho}}_{AB} = \mu_{AB} \left(\frac{\mathbf{P}_B}{m_B} - \frac{\mathbf{P}_A}{m_A} \right), \quad (8)$$

where the reduced mass is

$$\frac{1}{\mu_{AB}} = \frac{1}{m_A} + \frac{1}{m_B}. \quad (9)$$

The momentum of the ABC parent molecule is

$$\mathbf{p}_{ABC} = M \dot{\mathbf{X}} = \mathbf{P}_A + \mathbf{P}_B + \mathbf{P}_C. \quad (10)$$

Since we evaluate the momenta of all fragments in the parent molecule's CM frame, i.e. $\mathbf{p}_{ABC} = 0$, Eq. (6) simplifies to

$$\mathbf{p}_{AB,C} = \mathbf{P}_C. \quad (11)$$

Finally, we define the angle $\theta_{AB,C}$ between $\mathbf{p}_{AB,C}$ and $\mathbf{p}_{AB}$, shown in Fig. 2(b), as

$$\theta_{AB,C} = \cos^{-1} \left(\frac{\mathbf{p}_{AB,C} \cdot \mathbf{p}_{AB}}{|\mathbf{p}_{AB,C}| |\mathbf{p}_{AB}|} \right). \quad (12)$$

It is important to note that to analyze sequential breakup via a different intermediate, one still uses the same approach detailed above, but must choose the initial Jacobi set of specific interest. In the case of three body breakup, there are three possible choices for the Jacobi sets. In addition, the A, B, and C fragments may also represent molecular fragments. In this case, their corresponding momentum, e.g. $\mathbf{P}_A$, corresponds to the center-of-mass momentum of the molecular fragment.

B. Signature of sequential fragmentation

The key to identifying sequential breakup and then separating it from concerted fragmentation is a clear signature, which in this case is the rotation of the intermediate AB molecule in the fragmentation plane. To identify this signature of sequential fragmentation, the following two conditions must be valid:

1. The rotation of $\mathbf{p}_{AB}$ occurs in the fragmentation plane, with a normal vector defined by $\mathbf{p}_{AB} \times \mathbf{p}_{AB,C}$.
2. AB rotates long enough to “forget” its initial alignment with respect to the first fragmentation step given by $\mathbf{p}_{AB,C}$.

When both conditions are satisfied, the signature of sequential fragmentation is a nearly uniform $N(\theta_{AB,C})$ distribution, while concerted breakup is expected to be peaked about some $\theta_{AB,C}$. In Appendix A, we introduce a simple model explaining why the $N(\theta_{AB,C})$ distribution is not exactly uniform.

Another way to phrase the first condition is that the angular momentum of the AB intermediate, i.e. $\mathbf{J}_{AB}$, is parallel to the normal of the fragmentation plane. In the case of a bent triatomic molecule, all the atomic constituents must lie in the molecular plane. Therefore, using classical arguments and assuming central forces, the interaction between the C fragment and the intermediate AB molecule produces a torque, and hence angular momentum $\mathbf{J}_{AB}$ about the CM of AB, that is perpendicular to the molecular plane. As long as the mechanisms for producing angular momentum within the molecular

plane are minor, then the AB intermediate should rotate mostly within the fragmentation plane. Some examples of mechanisms that may induce angular momentum within the molecular plane are forces due to the electrons ejected during ionization, an asymmetric electron charge distribution above and below the molecular plane due to the interference of opposite parity states, or initial angular momentum due to the temperature of the target gas. Similar arguments are also expected to apply to (nearly) planar polyatomic molecules as long as the deformations out of the molecular plane before and/or during the fragmentation are small. In contrast, the first condition is unlikely to be satisfied for non-planar polyatomic molecules, which we hope to address in the future.

If the first condition is not met, the signature of sequential fragmentation changes. One extreme example is when the conjugate momentum describing the second step, $\mathbf{p}_{AB}$, rotates in a plane perpendicular to $\mathbf{p}_{AB,C}$. In this situation, all sequential fragmentation events are peaked at $\theta_{AB,C} = 90^\circ$ instead of forming a uniform $N(\theta_{AB,C})$ distribution. Similarly, the common signatures of sequential fragmentation in Dalitz plots and Newton diagrams also change.

Even though we observe a nearly uniform $N(\theta_{AB,C})$ distribution in the experiment presented in this paper, the exact criteria needed to satisfy the second condition are still under investigation. Specifically, in the future we plan to determine the relationship between the rotational period of the AB intermediate and the populated state's lifetime needed to produce a uniform distribution. Intuitively, we expect a uniform $N(\theta_{AB,C})$ distribution when the lifetime, τ , of the populated metastable state of the intermediate AB molecule is much longer than its rotational period T_R , i.e. $T_R \ll \tau$. We are still investigating the exact circumstances needed to produce a uniform $N(\theta_{AB,C})$ distribution in general.

To further distinguish sequential from concerted breakup, we plot the three-body breakup events as a function of $\theta_{AB,C}$ and the kinetic energy release (KER) in the second step, KER_{AB} , which is

$$\text{KER}_{AB} = \frac{\mathbf{p}_{AB}^2}{2\mu_{AB}}. \quad (13)$$

Since the internal energy of the intermediate AB molecule is independent of its final breakup angle $\theta_{AB,C}$, KER_{AB} is as well. Therefore, using the $N(\text{KER}_{AB}, \theta_{AB,C})$ distribution is a more differential and therefore a better test for identifying and further separating sequential breakup from other processes compared to the one-dimensional $N(\theta_{AB,C})$ distribution.

C. Determining the sequential fragmentation contributions in OCS

In this section, we study the three-body fragmentation of the OCS molecule using the native frames method

and identify sequential fragmentation by taking advantage of its signature, i.e., the rotation of the intermediate molecule in the fragmentation plane. Before plotting the $N(\text{KER}_{CO}, \theta_{CO,S})$ and $N(\text{KER}_{CS}, \theta_{CS,O})$ distributions, we first discuss why the rotation of the intermediate molecule is expected to occur mostly in the fragmentation plane.

As previously stated, since OCS is a triatomic molecule, all atomic constituents lie in the molecular plane assuming the molecule is slightly bent from its linear equilibrium geometry. In the case of sequential fragmentation involving a CO^{2+} intermediate, the C–S bond breaks in the first step, producing S^+ and CO^{2+} fragments. From a simple classical model assuming central forces, the charged S^+ then interacts with the dipole of the CO^{2+} molecule producing a torque, resulting in angular momentum perpendicular to the molecular plane. Modeling the interaction between an initially stationary point charge and a dipole, described in detail in Appendix B, the CO^{2+} may acquire more than $20\hbar$ of angular momentum for small variations from the linear geometry. As long as the CO^{2+} intermediate molecule gains little angular momentum within the OCS^{3+} molecular plane, its rotation will mostly occur in the fragmentation plane. For similar reasons, the rotation of the CS^{2+} intermediate should occur in the fragmentation plane as well.

To identify sequential fragmentation involving the CO^{2+} intermediate, we plot the $N(\text{KER}_{CO}, \theta_{CO,S})$ distribution for all events, shown in Fig. 3(a), where a uniform $N(\theta_{CO,S})$ distribution appears for $\theta_{CO,S} \lesssim 60^\circ$ centered at a $\text{KER}_{CO} \sim 6.5 \text{ eV}$. The $N(\theta_{CO,S})$ distribution integrated over all KER_{CO} , shown in Fig. 3(b), emphasizes that the distribution is uniform for $\theta_{CO,S} \lesssim 60^\circ$. Only a subset of $\theta_{CO,S}$ produces a uniform distribution since other competing processes, such as concerted breakup, overlap the sequential fragmentation events and create a peak, visible at $\theta_{CO,S} \sim 130^\circ$. To show that the uniform distribution reemerges from the competing processes at large angles, in Fig. 3(b) we also plot the $N(\theta_{CO,S})$ distribution integrated over $8 < \text{KER}_{CO} < 11 \text{ eV}$.

To determine if sequential fragmentation involving the CS^{2+} intermediate occurs, we plot in Figs. 3(c) and (d), respectively, the $N(\text{KER}_{CS}, \theta_{CS,O})$ and $N(\theta_{CS,O})$ distributions for all events. In these plots, we identify sequential fragmentation as a uniform $N(\theta_{CS,O})$ distribution for $\theta_{CS,O} \lesssim 60^\circ$ centered at $\text{KER}_{CS} \sim 5.5 \text{ eV}$. Later, in Section VIA, we show that sequential fragmentation involving the CO^{2+} fragment and concerted breakup both contribute in forming a peak at $\theta_{CS,O} \sim 120^\circ$.

Unfortunately, the $N(\theta_{CO,S})$ and $N(\theta_{CS,O})$ distributions, shown in Fig. 3, are not perfectly uniform, with ‘dips’ occurring at 0° and 180° . One possible source of the ‘dips’ is a consequence of using a polar angle $\theta_{AB,C}$ to describe the rotation of the AB intermediate, which forms a uniform distribution in a ring with finite thickness, as we explain further in Appendix A. However, an experimental artifact due to the reduced efficiency

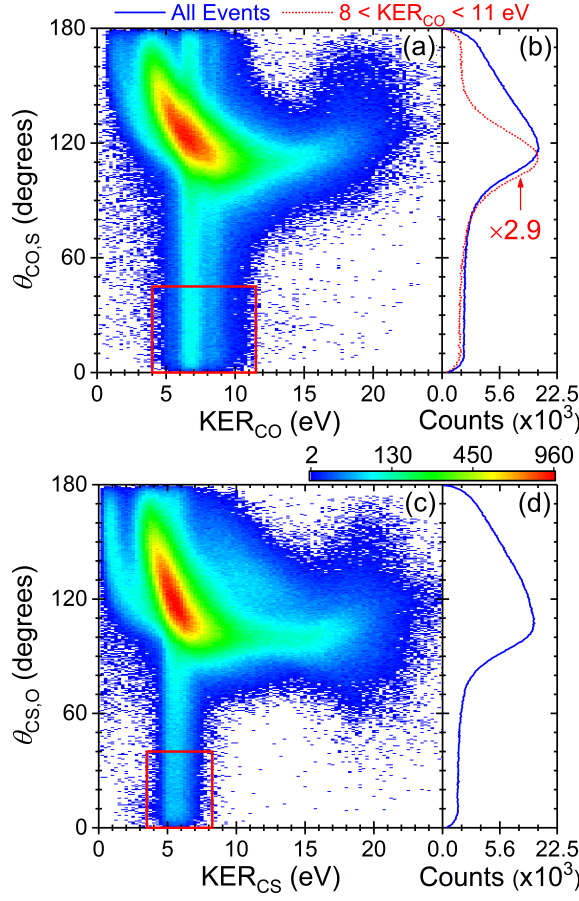


FIG. 3. (Color online) All $O^+ + C^+ + S^+$ events as a function of (a) KER_{CO} and $\theta_{CO,S}$, (b) $\theta_{CO,S}$, (c) KER_{CS} and $\theta_{CS,O}$, and (d) $\theta_{CS,O}$. The $N(\theta_{CO,S})$ distributions in (b) are integrated over all KER_{CO} (blue curve) and $8 \leq KER_{CO} \leq 11$ eV (red curve), while the $N(\theta_{CS,O})$ distribution in (d) is integrated over all KER_{CS} (blue curve). Note that the error bars of the $N(\theta_{CO,S})$ and $N(\theta_{CS,O})$ distributions appear as shaded regions, which is the style used throughout this paper. In this figure, the error bars are approximately the thickness of the line. The red rectangles define the regions used in Section IV to select sequential fragmentation events.

near the center of the position sensitive detector may also contribute to these ‘dips.’ Specifically, the lower efficiency region on the detector is caused by the high rate of OCS^{q+} molecules and He ions from the carrier gas. In the case of sequential fragmentation via a CO^{2+} intermediate, the O^+ fragment has a small kinetic energy when $\theta_{CO,S} = 0^\circ$ because it is ejected in the opposite direction of the CO^{2+} molecule’s center-of-mass. On the other hand, the C^+ fragment has a similarly small kinetic energy when $\theta_{CO,S} = 180^\circ$. As a result, these fragments do not have enough momentum parallel to the detector plane to escape the inefficient detector regions regardless of the laser’s polarization direction, potentially contributing to the ‘dips’ at the edges of the $N(\theta_{CO,S})$ distribution. Fortunately, since the ‘dips’ only affect a

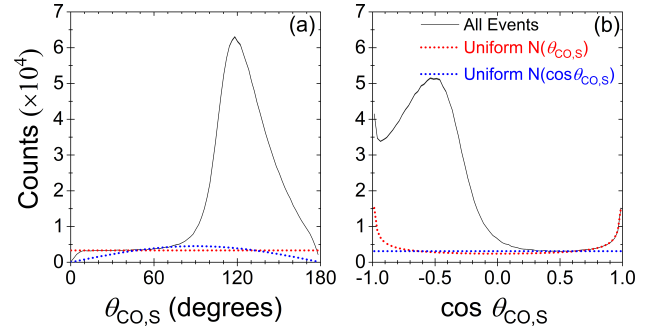


FIG. 4. (Color online) All $O^+ + C^+ + S^+$ events plotted as a function of (a) $\theta_{CO,S}$ and (b) $\cos \theta_{CO,S}$. In addition, the red and blue lines show the functional forms of uniform $N(\theta_{CO,S})$ and $N(\cos \theta_{CO,S})$ distributions, respectively (see text).

small part of the $N(\theta_{CO,S})$ and $N(\theta_{CS,O})$ distributions, the native-frames method can still be applied.

A valid question to ask is why sequential fragmentation is uniform in $\theta_{AB,C}$ instead of $\cos \theta_{AB,C}$ since $\theta_{AB,C}$ is a polar angle in the body-fixed frame, shown in Fig. 2(b). In general, three-dimensional distributions are plotted as a function of $\cos \theta$ since isotropic spherical distributions produce a uniform $N(\cos \theta)$ distribution. In the case of sequential fragmentation, the conjugate momentum corresponding to the second fragmentation step, $\mathbf{p}_{AB}$, predominantly rotates in a plane, producing a uniform angular distribution along a ring instead of a sphere. Therefore, we plot $\theta_{AB,C}$ instead of $\cos \theta_{AB,C}$ (see Appendix A).

To demonstrate this point, we plot the $N(\theta_{CO,S})$ and $N(\cos \theta_{CO,S})$ distributions for all events in Fig. 4(a) and Fig. 4(b), respectively. In addition, we plot the functional forms of uniform distributions in $N(\theta_{CO,S})$ and $N(\cos \theta_{CO,S})$ (red and blue dotted lines, respectively). In Fig. 4(a), the uniform $N(\theta_{CO,S})$ distribution fits the data nicely, while the uniform $N(\cos \theta_{CO,S})$ distribution does not [80]. Similarly, Fig. 4(b) shows that the uniform $N(\theta_{CO,S})$ distribution fits the data best [81].

Therefore, in the case of the sequential three-body fragmentation of the OCS molecule into $O^+ + C^+ + S^+$, the signature of sequential fragmentation via the CO^{2+} and CS^{2+} intermediates are uniform $N(\theta_{CO,S})$ and $N(\theta_{CS,O})$ distributions, respectively.

D. Euler angle analysis

In this section, we perform some additional analysis to study the alignment of the fragmentation plane in space using Euler angles for the events contributing to sequential breakup. In particular, we expect that the $N(\theta_{AB,C})$ distribution should be uniform for any orientation of the fragmentation plane in space since the rotation of the intermediate molecule predominantly occurs in that plane. Note, to gain information from this approach, the breakup needs to have a preferential align-

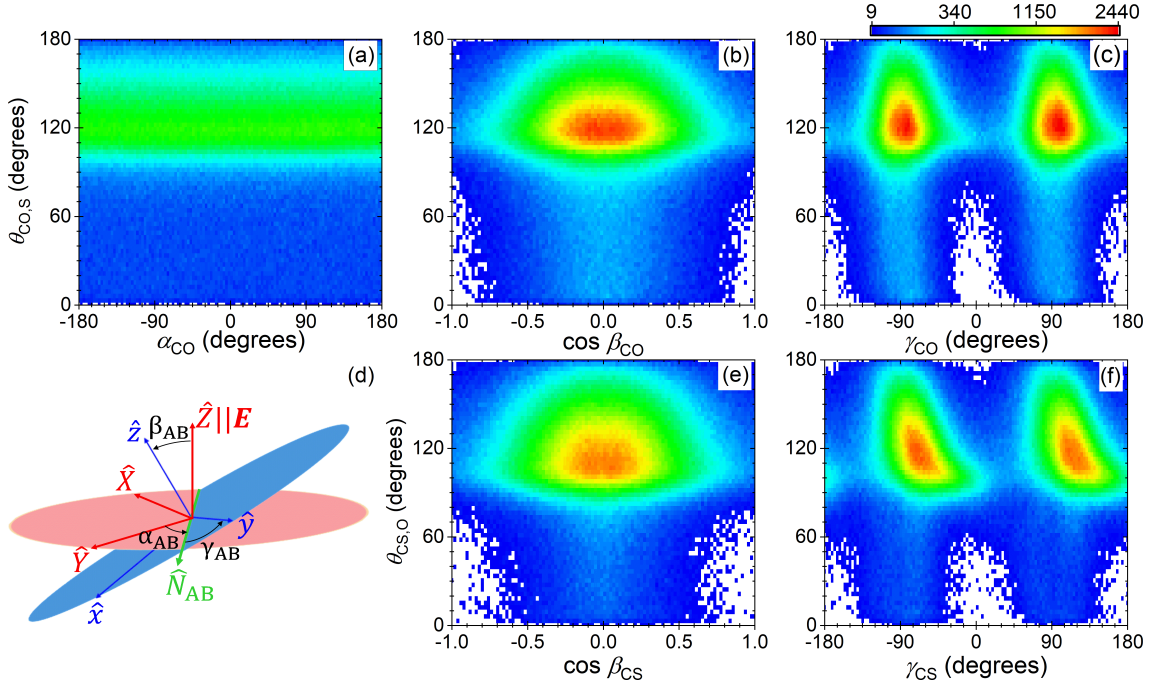


FIG. 5. (Color online) All $O^+ + C^+ + S^+$ events as a function of (a) α_{CO} and $\theta_{CO,S}$, (b) $\cos \beta_{CO}$ and $\theta_{CO,S}$, and (c) γ_{CO} and $\theta_{CO,S}$, which represent the alignment of the fragmentation plane for sequential fragmentation via the CO^{2+} intermediate. (d) A schematic displaying the Euler angles for sequential fragmentation via an arbitrary AB molecule. All $O^+ + C^+ + S^+$ events as a function of (e) $\cos \beta_{CS}$ and $\theta_{CS,O}$, and (f) γ_{CS} and $\theta_{CS,O}$ for sequential fragmentation involving the CS^{2+} intermediate.

ment in space, which is the case for the strong-field triple ionization and fragmentation of OCS (see Sec. IV A).

To define the Euler angles, we begin with the lab-fixed XYZ coordinate system, where we fix the $\hat{Z}$ axis along the laser polarization, the $\hat{Y}$ axis is parallel to the laser propagation direction, and $\hat{X}$ is chosen to form a right-handed coordinate system. Additionally, we define the body-fixed xyz axes for sequential breakup involving the intermediate AB molecule, shown in Fig. 5(d), as

$$\hat{z}_{AB} = \frac{\mathbf{p}_{AB,C} \times \mathbf{p}_{AB}}{|\mathbf{p}_{AB,C} \times \mathbf{p}_{AB}|}, \quad (14)$$

which is the normal of the fragmentation plane, while the axes within the plane are

$$\hat{y}_{AB} = \frac{\mathbf{p}_{AB,C}}{|\mathbf{p}_{AB,C}|}, \quad (15)$$

and

$$\hat{x}_{AB} = \frac{\hat{y}_{AB} \times \hat{z}_{AB}}{|\hat{y}_{AB} \times \hat{z}_{AB}|}. \quad (16)$$

The Euler angles α_{AB} , β_{AB} , and γ_{AB} are shown pictorially in Fig. 5(d). The angle α_{AB} is defined as

$$\alpha_{AB} = \tan^{-1} \left(-\frac{\hat{N}_{AB} \cdot \hat{X}}{\hat{N}_{AB} \cdot \hat{Y}} \right), \quad (17)$$

where the line of nodes $\hat{N}_{AB}$ is

$$\hat{N}_{AB} = \frac{\hat{Z} \times \hat{z}_{AB}}{|\hat{Z} \times \hat{z}_{AB}|}. \quad (18)$$

Physically, α_{AB} is the angle between $\hat{N}_{AB}$ (the intersection between the xy and XY planes) and the Y axis. Since $\hat{N}_{AB}$ is always perpendicular to the projection of $\hat{z}_{AB}$ into the XY plane, α_{AB} represents the azimuthal angle of $\hat{z}_{AB}$ about the laser polarization (Z axis). Due to the symmetries about the laser polarization, the $N(\alpha_{AB})$ distribution should be uniform. The angle β_{AB} is the angle between the normal to the fragmentation plane and the laser polarization given by

$$\cos \beta_{AB} = \hat{Z} \cdot \hat{z}_{AB}. \quad (19)$$

Finally, γ_{AB} is

$$\gamma_{AB} = \tan^{-1} \left(\frac{\hat{N}_{AB} \cdot \hat{x}_{AB}}{\hat{N}_{AB} \cdot \hat{y}_{AB}} \right). \quad (20)$$

where $\mathbf{p}_{AB,C}$ lies along the projection of the laser polarization into the fragmentation plane when $\gamma_{AB} = \pm 90^\circ$. In other words, γ_{AB} provides information about the relative angle between $\mathbf{p}_{AB,C}$ and the projection of the laser polarization into the fragmentation plane.

In Fig. 5(a-c), we show density plots of all $O^+ + C^+ + S^+$ events in the reference frame of a CO^{2+}

intermediate as a function of the individual Euler angles and $\theta_{\text{CO},S}$. Note that in each plot, we integrate over all other degrees of freedom not shown in the figure, such as the remaining Euler angles and KER. To demonstrate that sequential fragmentation involving the CO^{2+} intermediate produces a uniform $N(\theta_{\text{CO},S})$ distribution for any spatial orientation of the fragmentation plane, we must recall that sequential breakup is only separated for $\theta_{\text{CO},S} \lesssim 60^\circ$ while larger angles also contain other competing processes. Therefore, we only expect the $N(\alpha_{\text{CO}}, \theta_{\text{CO},S})$, $N(\cos \beta_{\text{CO}}, \theta_{\text{CO},S})$, and $N(\gamma_{\text{CO}}, \theta_{\text{CO},S})$ distributions, shown in Fig. 5(a-c), to be uniform only for $\theta_{\text{CO},S} \lesssim 60^\circ$.

The density plots of all $\text{O}^+ + \text{C}^+ + \text{S}^+$ events as a function of the Euler angles and $\theta_{\text{CS},O}$ similarly show that sequential fragmentation involving the CS^{2+} intermediate's $N(\theta_{\text{CS},O})$ distribution is uniform for any fragmentation plane's orientation in space, as shown in Fig. 5(e-f) for $\theta_{\text{CS},O} \lesssim 60^\circ$. Note that we do not plot $N(\alpha_{\text{CS}}, \theta_{\text{CS},O})$, which yields a nearly identical plot to Fig. 5(a), because the breakup is uniform due to the azimuthal symmetry about the linearly polarized field.

In Section VID, we use the Euler angles, in conjunction with other aspects of the native-frames method, to show that sequential fragmentation via the SO^{2+} intermediate does not occur in our experiment.

The Euler angles also contain information about the spatial alignment of the sequential fragmentation events. For example, the $N(\cos \beta_{\text{CO}})$ and $N(\cos \beta_{\text{CS}})$ distributions for sequential breakup (at $\theta_{\text{AB},C} \leq 60^\circ$), shown in Fig. 5(b) and Fig. 5(e), respectively, demonstrate that the laser polarization is preferentially within the fragmentation plane since both distributions are peaked at $\cos \beta = 0$. Additionally, the $N(\gamma_{\text{CO}})$ and $N(\gamma_{\text{CS}})$ distributions, shown in Fig. 5(c) and Fig. 5(f), respectively, show that the first step of sequential fragmentation (again, at angles $\theta_{\text{AB},C} \leq 60^\circ$) tends to roughly align along the projection of the polarization axis ($\hat{Z}$) into the fragmentation plane since the distributions are peaked at $\gamma = \pm 90^\circ$.

IV. UNDERSTANDING SEQUENTIAL FRAGMENTATION

After identifying sequential fragmentation, we can extract information about the first and second fragmentation steps of the sequential breakup, such as kinetic energy released in each step, as well as determine the branching ratios of sequential versus concerted breakup. We discuss how to retrieve such information in the following section.

A. Sequential fragmentation – first step

Here, we compare the first step of sequential three-body fragmentation via the CO^{2+} and CS^{2+} intermedi-

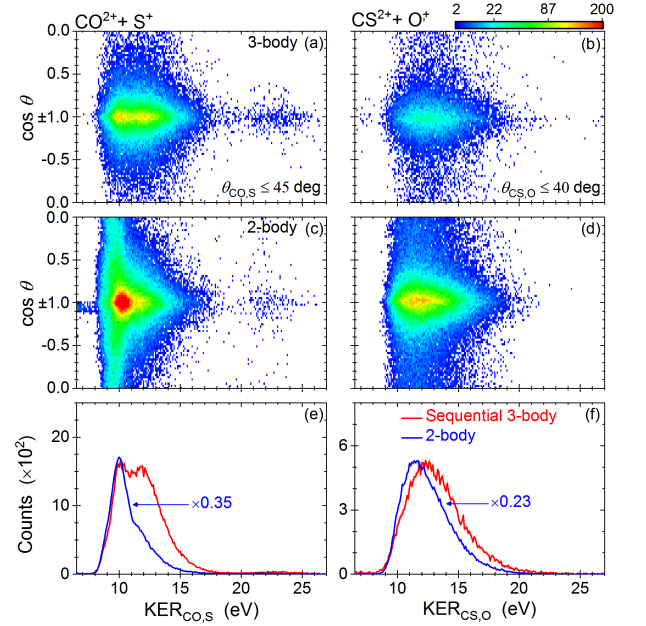


FIG. 6. (Color online) Sequential fragmentation events via $\text{CO}^{2+} + \text{S}^+$ (left column) and $\text{CS}^{2+} + \text{O}^+$ (right column) plotted as a function of (a) $\text{KER}_{\text{CO},S}$ and $\cos \theta$, and (b) $\text{KER}_{\text{CS},O}$ and $\cos \theta$ for the regions $\theta_{\text{CO},S} \leq 45^\circ$ and $\theta_{\text{CS},O} \leq 40^\circ$, respectively. The angle θ is defined in Eq. 22. The two-body fragmentation via $\text{CO}^{2+} + \text{S}^+$ and $\text{CS}^{2+} + \text{O}^+$, associated with their respective sequential breakup, as a function of (c) $\text{KER}_{\text{CO},S}$ and $\cos \theta$, and (d) $\text{KER}_{\text{CS},O}$ and $\cos \theta$, respectively. The (e) $N(\text{KER}_{\text{CO},S})$ and (f) $N(\text{KER}_{\text{CS},O})$ distributions integrated over $\cos \theta$.

ate molecules to the two-body $\text{CO}^{2+} + \text{S}^+$ and $\text{CS}^{2+} + \text{O}^+$ breakup channels, respectively. The motivation behind this comparison is the assessment that two-body breakup, via $\text{CO}^{2+} + \text{S}^+$ and $\text{CS}^{2+} + \text{O}^+$, is similar to the first step in sequential three-body fragmentation, but in which the intermediate dication survives intact all the way to the detector. By contrasting the KER distributions, we learn about the differences between the populated states leading to each outcome.

Returning to the ABC notation, the KER of the first fragmentation step is

$$\text{KER}_{\text{AB},C} = \frac{p_{\text{AB},C}^2}{2\mu_{\text{AB},C}}. \quad (21)$$

In addition, the angle θ of the first-step conjugate momentum with respect to the laser polarization, $\hat{Z}$, is

$$\cos \theta = \frac{p_{\text{AB},C} \cdot \hat{Z}}{|p_{\text{AB},C}|}. \quad (22)$$

The $N(\text{KER}_{\text{AB},C}, \cos \theta)$ distributions for the three-body sequential fragmentation channels involving the intermediate CO^{2+} and CS^{2+} molecules are shown in Fig. 6(a) and Fig. 6(b), respectively. Note that to make these plots, we select the sequential fragmentation events

in the regions where $\theta_{\text{CO,S}} \leq 45^\circ$ and $\theta_{\text{CS,O}} \leq 40^\circ$ for the CO^{2+} and CS^{2+} intermediates, respectively. For comparison, the distributions of the two-body breakup channels, $\text{CO}^{2+} + \text{S}^+$ and $\text{CS}^{2+} + \text{O}^+$, are presented in Fig. 6(c) and Fig. 6(d), respectively. The associated $\text{KER}_{\text{AB,C}}$ distributions integrated over all other degrees of freedom are shown in Fig. 6(e-f). The three-body and two-body distributions look similar, especially the angular distributions that exhibit a strong alignment preference along the laser polarization.

One notable difference is that the three-body sequential breakup extends to higher KER than the two-body breakup, as indicated by Fig. 6(e-f), especially for the $\text{CO}^{2+} + \text{S}^+$ channel. This KER measures the energy difference between the OCS^{3+} state populated by triple ionization and the $\text{CO}^{2+} + \text{S}^+$ [or $\text{CS}^{2+} + \text{O}^+$] dissociation limit (note that these dissociation limits are bands in energy because of the internal, rovibrational, energy of the intact intermediate). Given that the internal energy spread of the CO^{2+} states that survive all the way to the detector is small, i.e. less than 0.23 eV [82–84] [0.52 eV for CS^{2+} [85]], the dissociation-limit spread is too small to cause the difference in the $\text{KER}_{\text{CO,S}}$ distributions observed in Fig. 6(e). Therefore, we expect higher states of OCS^{3+} to be responsible for the higher KER tail in the sequential three-body breakup.

In addition, careful inspection of Fig. 6(e-f) indicates that the $\text{KER}_{\text{CS,O}}$ distribution is shifted up with respect to the $\text{KER}_{\text{CO,S}}$ distribution by about 1.3 eV. This energy shift matches the difference between the dissociation limits of the $\text{CO}^{2+} + \text{S}^+$ and $\text{CS}^{2+} + \text{O}^+$ channels in their lowest rovibrational state of the ground $X^3\Pi$ electronic state [85, 86]. This suggests that each sequential fragmentation pathway leading to $\text{O}^+ + \text{C}^+ + \text{S}^+$ may originate at the same energy on the potential energy surfaces of the transient OCS^{3+} molecule, but break along different reaction coordinates.

To further explore this point, we plot the energy of the sequential three-body breakup in Fig. 7, where $E=0$ represents the energy of the ground $X^1\Sigma^+(v=0,0,0)$ state of the neutral OCS molecule. The energy scale in Fig. 7 is equivalent to the one used in the potential energy plots reported by Eland *et al.* [87], allowing us to determine which OCS^{3+} states contribute. Assuming that the fragmentation ends on the lowest dissociation limit, i.e. $\text{O}^+(^4S) + \text{C}^+(^2P) + \text{S}^+(^4S)$, we compute the excitation energy with respect to the OCS ground state, $X^1\Sigma^+(v=0,0,0)$, by summing the KER, the ionization energies of each atomic fragment [88], as well as the dissociation energies of the $\text{OCS}(X^1\Sigma^+)$ ground state into $\text{CO}(X^1\Sigma^+(v=0)) + \text{S}(^3P)$ [89] and $\text{CO}(X^1\Sigma^+(v=0))$ into $\text{C}(^3P) + \text{O}(^3P)$ [90]. Note that the KER mentioned above is given by

$$\text{KER} = \text{KER}_{\text{AB,C}} + \text{KER}_{\text{AB}}, \quad (23)$$

i.e., the energy release in the two fragmentation steps.

In Fig. 7, we see that the energy distributions for both three-body sequential processes overlap, reinforcing the

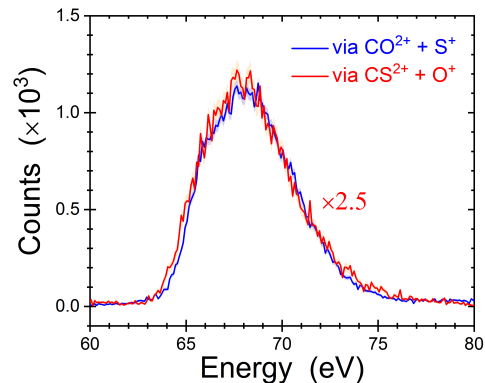


FIG. 7. (Color online) The energy distributions of sequential three-body fragmentation via the CO^{2+} and CS^{2+} intermediates. We select the relevant event using the, respective, $\theta_{\text{CO,S}} \leq 45^\circ$ and $\theta_{\text{CS,O}} \leq 40^\circ$ conditions. Zero energy is set at the ground state, $X^1\Sigma^+(v=0,0,0)$, of the OCS molecule.

idea that both sequential breakup processes begin on the same group of potential energy surfaces. Then, asymmetric stretch of the O–C or C–S bond on each potential surface may lead to CS^{2+} or CO^{2+} intermediate, respectively, in the first step. We note that the OCS^{3+} ground state is about ~ 61 eV above the OCS ground state at the equilibrium geometry (and even lower for stretched or bent OCS geometry) [87]. This energy is significantly lower than the measured energy, shown in Fig. 7, suggesting that the OCS^{3+} ground state does not contribute significantly to the sequential breakup in our measurements. On the other hand, the measured energy distribution, and in particular its width, are consistent with contributions from a group of low-lying excited states of OCS^{3+} . The relative importance of each of these states and their specific energy spectrum require theoretical treatment that is beyond the scope of our work.

B. Sequential fragmentation – second step

Plots of the second step KER distribution, i.e. $N(\text{KER}_{\text{AB}})$, are useful for determining the internal energy of the metastable AB intermediate. In Fig. 8(a), we show the $N(\text{KER}_{\text{AB}})$ distribution for $\theta_{\text{CO,S}} \leq 45^\circ$, which only contains sequential fragmentation events involving the CO^{2+} intermediate. In addition, we include tick marks representing the expected KER_{CO} associated with field free vibrational states of the four lowest electronic states of CO^{2+} for $J=1$. Aside from the lower comb of $A^3\Sigma^+$ vibrational states, the calculation of the KER_{CO} of each vibrational state assumes predissociation to the lowest asymptotic limit of CO^{2+} . For example, one possible pathway is via spin-orbit coupling to the repulsive $^3\Sigma^-$ state. In contrast, the lower comb of $A^3\Sigma^+$ vibrational states assumes fragmentation leading to the first excited $\text{C}^+(^2P) + \text{O}^+(^2D)$ dissociation limit, which can occur via spin-orbit coupling through the $c^1\Delta$ state.

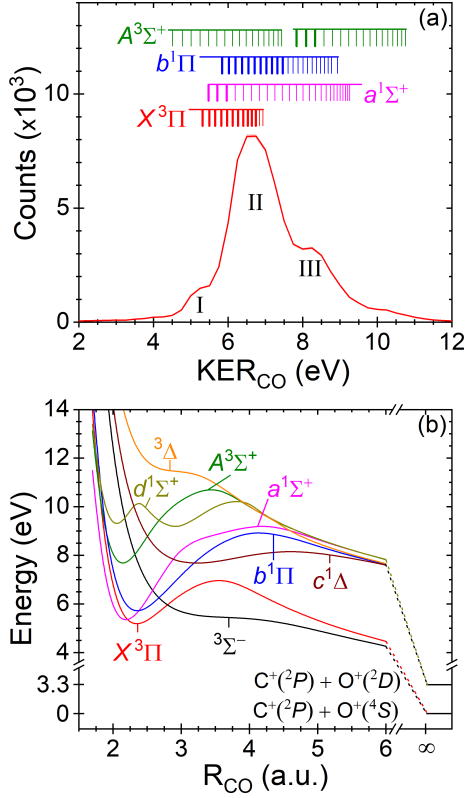


FIG. 8. (Color online) (a) Sequential fragmentation events via the CO^{2+} intermediate as a function of KER_{CO} for $\theta_{\text{CO,S}} \leq 45^\circ$. The expected field-free KER of the vibrational states of the four lowest lying electronic states are depicted by the tick marks. Specifically, the thick tick marks are based on high-resolution spectroscopy by Lundqvist *et al.* [83] with the assignment correction noted by Hochlaf *et al.* [84]. For the low-lying states not measured in the previous experiments [83, 84], the vertical photoionization energies provided by Dawber *et al.* [91] are used. The thin tick marks are calculated using the phase amplitude method [92] for $J = 1$ and the potential energy curves provided in Ref. [86]. (b) The potential energy curves of CO^{2+} (adapted from Ref. [86]).

For an electronic state to contribute to the measured $N(\text{KER}_{\text{CO}})$ distribution, the rovibrational state's lifetime must fall within a certain time window. The upper limit is related to the flight time of the CO^{2+} and CS^{2+} intermediate molecules to the detector, which in our experiment is approximately $3 \mu\text{s}$. Using momentum conservation we can exclude events in which the intermediate molecule, CO^{2+} for example, significantly move in the spectrometer before dissociating. We estimate that such events of CO^{2+} dissociation in flight can be separated if the flight time is longer than 200 ns. Therefore, contributions from states with longer lifetimes will be significantly suppressed, for example, only 5% of the population of a state with $\tau = 3 \mu\text{s}$ may contribute to the $N(\text{KER}_{\text{CO}})$ distribution.

On the other hand, the lowest lifetime depends on the ratio between the intermediate molecule's rotational pe-

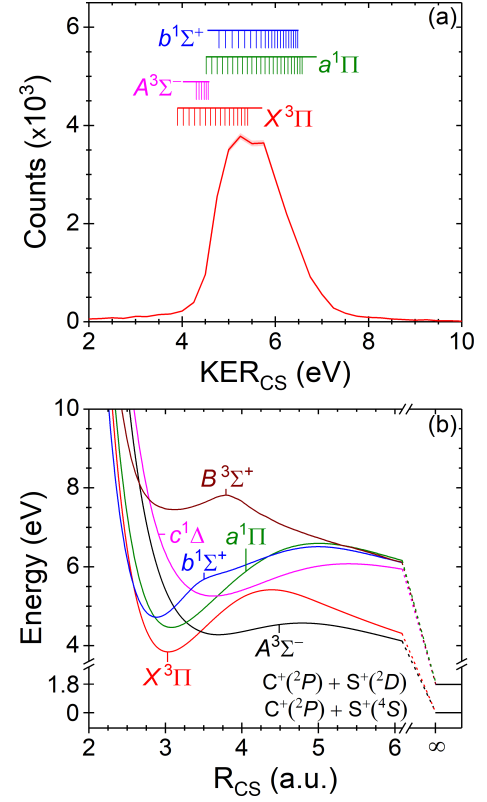


FIG. 9. (Color online) (a) Sequential fragmentation events via the CS^{2+} intermediate as a function of KER_{CS} for $\theta_{\text{CS,O}} \leq 40^\circ$. The expected field-free KER of the vibrational states of the four lowest lying electronic states are depicted by the tick marks, which we calculated using the phase amplitude method [92] for the potential energy curves reported in Ref. [85]. (b) The potential energy curves of CS^{2+} (adapted from Ref. [85]).

riod, T_R , and τ . If $T_R \ll \tau$, then we expect to observe a uniform $N(\theta_{\text{AB,C}})$ distribution as long as the rotation occurs in the fragmentation plane. The exact relationship between T_R and τ needed to produce a uniform $N(\theta_{\text{AB,C}})$ distribution is still under investigation. It is worth noting that for large angular momentum the rotational period decreases. For example, if $J = 20$, $T_R \approx 450$ fs for the ground $X^3\Pi(v=0)$ state, as compared to $T_R \approx 9$ ps for $J = 1$. This suggests that states with higher J and lifetimes of several hundreds femtoseconds to a few picoseconds can contribute to the measured $N(\text{KER}_{\text{CO}})$ distributions.

For the sake of discussing which rovibrational states may contribute to the $N(\text{KER}_{\text{CO}})$ distribution, we limit the discussion to $J = 1$ ($T \sim 9$ ps for $v = 0$ in the ground $X^3\Pi$ state) since calculations for high J values are not readily available for the CO^{2+} and CS^{2+} molecules and predissociation lifetimes depend on J [93, 94]. Following the arguments above, the $X^3\Pi(v=0)$ state does not contribute significantly to the measured $N(\text{KER}_{\text{CO}})$ distribution, since its lifetime is on the order of 7 ms [82].

TABLE I. The branching ratios for the sequential and concerted fragmentation processes.

Step	Sequential $\text{CO}^{2+} + \text{S}^+$		Concerted $\text{O}^+ + \text{C}^+ + \text{S}^+$	Sequential $\text{CS}^{2+} + \text{O}^+$	
1 st	$19.88 \pm 0.82\%$		$69.90 \pm 0.72\%$	$10.22 \pm 0.63\%$	
2 nd	$\text{CO}^{2+} + \text{S}^+$	$\text{O}^+ + \text{C}^+ + \text{S}^+$		$\text{O}^+ + \text{C}^+ + \text{S}^+$	$\text{CS}^{2+} + \text{O}^+$
	$2.61 \pm 0.79\%$	$17.27 \pm 0.19\%$	$69.90 \pm 0.72\%$	$2.05 \pm 0.62\%$	$8.17 \pm 0.10\%$

The remaining vibrational states of the $X^3\Pi$ and $a^1\Sigma^+$ states as well as the $b^1\Pi$ state may contribute to the dominant KER_{CO} peak, labeled as II in Fig. 8(a). However, our predissociation rate calculations (see Ref. [82] for method) suggest that the $(v, J) = (4, 1)$ state of the $X^3\Pi$ electronic state may not contribute since its lifetime is below 1 ps. Other rovibrational states of these electronic states may have lifetimes too short to contribute to the KER_{CO} distribution. The high KER_{CO} peak, labeled as III in Fig. 8(a), may be associated with the high-lying vibrational states of the $a^1\Sigma^+$ and $b^1\Pi$ states as well as the low-lying vibrational states of the $A^3\Sigma^+$ state.

To identify states responsible for the low KER_{CO} shoulder, labeled as I in Fig. 8(a), higher excited states of the CO^{2+} intermediate molecule that predissociate to the first excited $\text{C}^+ (^2P) + \text{O}^+ (^2D)$ limit must be considered. One possible electronic state is the $A^3\Sigma^+$ with vibrational states that can predissociate through spin-orbit coupling to the $c^1\Delta$ state, which is represented by the low KER_{CO} set of tick marks associated with the $A^3\Sigma^+$ state in Fig. 8(a). Higher lying vibrational states of the $a^1\Sigma^+$ and the $b^1\Pi$ may also predissociate via the $c^1\Delta$ state leading to energies that may contribute to the lowest KER_{CO} peak.

Similarly for fragmentation via the CS^{2+} intermediate, Fig. 9(a) shows the $N(\text{KER}_{\text{CS}})$ distribution for $\theta_{\text{CS},\text{O}} \leq 40^\circ$, shown as the red rectangle in Fig. 3(c). Here too, the tick marks represent the expected KER_{CS} for various vibrational and electronic states of CS^{2+} with $J=1$. Using similar arguments to those provided for the CO^{2+} intermediate and the reported lifetimes of the CS^{2+} molecule [85], we can determine the relevant states that contribute to the measured $N(\text{KER}_{\text{CS}})$ distribution. In particular, the high-lying vibrational states of $X^3\Pi$ and most vibrational states of the $a^1\Pi$ and $b^1\Sigma^+$ states contribute to the main KER_{CS} peak while the $A^3\Sigma^-$ state may only contribute to the low-energy shoulder.

C. Branching ratios

One advantage of the native-frames method over Newton diagrams and Dalitz plots is that it allows us a straightforward way to evaluate the branching ratios of the competing concerted and sequential breakup processes by exploiting the uniform $N(\theta_{\text{AB},\text{C}})$ distribution.

Assuming that $N(\theta_{\text{AB},\text{C}})$ is uniform over all $\theta_{\text{AB},\text{C}}$, the total number of sequential fragmentation events involv-

ing an AB molecule is

$$N_{\text{AB},\text{C}} = \frac{180}{\theta_{\text{max}} - \theta_{\text{min}}} \sum_{\theta_{\text{min}}}^{\theta_{\text{max}}} N(\theta_{\text{AB},\text{C}}), \quad (24)$$

where $[\theta_{\text{min}}, \theta_{\text{max}}]$ is the region where the sequential fragmentation events do not overlap with other channels. To determine the number of concerted fragmentation events, $N_{\text{conc.}}$, we subtract the number of events in all sequential fragmentation channels, i.e. all possible permutations of possible intermediate molecules, from the total number of three-body breakup events.

As previously mentioned, the assumption that $N(\theta_{\text{AB},\text{C}})$ is uniform for all $\theta_{\text{AB},\text{C}}$ is not exactly fulfilled in our experiment since ‘dips’ exist around $\theta_{\text{AB},\text{C}} = 0^\circ$ and 180° for both sequential processes. Furthermore, in Appendix A we provide a simple model describing one possible origin for the ‘dips’. This model also shows that the $N(\theta_{\text{AB},\text{C}})$ distribution as well as the ‘dips’ are symmetric about 90° . Therefore, to accurately determine the number of sequential events, we need to take the ‘dips’ into account. To do so, we select the region $[\theta_{\text{low}}, \theta_{\text{high}}]$ shown in Fig. 10(a) [95], which only include the dips and the region $[\theta_{\text{min}}, \theta_{\text{max}}]$ that selects the remaining separated sequential fragmentation events outside of the dips. Then, taking advantage of the reflection symmetry of $N(\theta_{\text{AB},\text{C}})$ about 90° , the total corrected number of sequential events are

$$N'_{\text{AB},\text{C}} = \frac{180 - 2(\theta_{\text{high}} - \theta_{\text{low}})}{\theta_{\text{max}} - \theta_{\text{min}}} \sum_{\theta_{\text{min}}}^{\theta_{\text{max}}} N(\theta_{\text{AB},\text{C}}) + 2 \sum_{\theta_{\text{low}}}^{\theta_{\text{high}}} N(\theta_{\text{AB},\text{C}}). \quad (25)$$

Then, $N_{\text{conc.}}$ is determined by subtracting $N'_{\text{AB},\text{C}}$ for all sequential breakup channels from the total number of three-body fragmentation events.

We report the evaluated branching ratios in Table I. Note that the two- and three-body breakup channels, are corrected for their different detection efficiency, specifically (ϵ^2) and (ϵ^3) , respectively. The single ion detection efficiency is estimated to be $\epsilon = 0.37 \pm 0.03$, by comparing the measured $\text{O}^+ + \text{C}^+ + \text{S}^+$ to the $\text{C}^+ + \text{S}^+$ ion-pairs measured in coincidence, i.e. events where the O^+ fragment was “lost”, as further explained in Ref. [96]. The reported errors in Table I include the statistical errors and the uncertainty in the detection efficiency.

Following triple ionization, the OCS molecule undergoes concerted three-body fragmentation into $O^+ + C^+ + S^+$ or sequential breakup, which is initiated by breaking into either $CO^{2+} + S^+$ or $CS^{2+} + O^+$ in the first breakup step. In the second step, the sequential fragmentation channels can either break into $O^+ + C^+ + S^+$ or the dication remains intact all the way to the detector. Sequential fragmentation involving the SO^{2+} molecule is not observed in our measurement (see further discussion in Section VID).

V. SEQUENTIAL FRAGMENTATION RETRIEVAL ALGORITHM

The main advantage of analyzing three-body breakup using native frames and identifying sequential breakup as a uniform angular $N(\theta_{AB,C})$ distribution is our ability to reconstruct the concealed sequential events by exploiting the uniform distribution. Below, we present an algorithm that reconstructs the whole sequential fragmentation distribution event-by-event, which allows one to separate competing sequential and concerted breakup in any plot created from the measured momenta. It is important to note that the reconstruction algorithm assumes that the rotation of the intermediate fragment occurs entirely in the fragmentation plane, which is not necessarily expected to be the case as explained in Section III.

Returning to the general ABC notation, our algorithm begins with selecting the clearly separated sequential

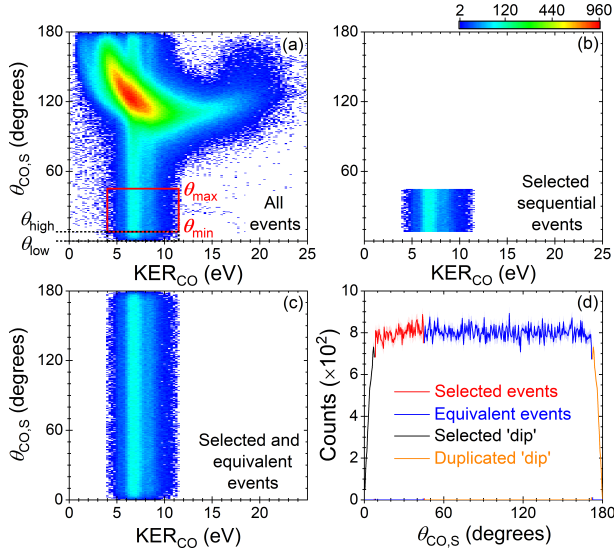


FIG. 10. (Color online) The $N(KER_{CO}, \theta_{CO,S})$ distributions for (a) all $O^+ + C^+ + S^+$ events, (b) the selected sequential events used to generate equivalent events, (c) the full sequential fragmentation distribution including the selected and reconstructed equivalent events, and (d) the $N(\theta_{CO,S})$ distributions for the different steps of the reconstruction algorithm integrated over KER_{CO} .

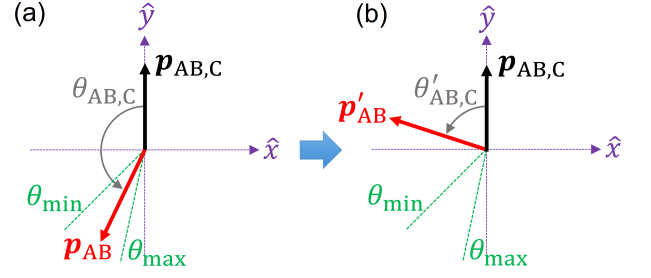


FIG. 11. (Color online) A schematic for reconstructing equivalent events. (a) an original measured sequential event is depicted (see text). (b) an equivalent event, which is just the original event rotated to a new, randomly generated, $\theta'_{AB,C}$ angle. Note that p_{AB} only spans the space for $x \leq 0$ due to the definition of the fragmentation plane.

events. Explicitly, we select the events within the range $\theta_{AB,C} = [\theta_{\min}, \theta_{\max}]$ and $KER_{AB} = [KER_{\min}, KER_{\max}]$. For example, the specific region used to select sequential fragmentation involving the CO^{2+} intermediate is $\theta_{CO,S} = [8^\circ, 45^\circ]$ and $KER_{CO} = [4, 11.5]$ eV, shown as the red rectangle in Fig. 10(a). The reconstruction of sequential fragmentation involving the CS^{2+} intermediate yields a similar figure (not shown for brevity) [?].

The goal of the algorithm is to generate equivalent events from the measured events and reproduce the sequential fragmentation distributions in regions overlapping other competing processes. To determine how many equivalent sequential events must be generated from a single measured event within $[\theta_{\min}, \theta_{\max}]$, we define the factor

$$F = \frac{180 - (\theta_{\max} - \theta_{\min})}{\theta_{\max} - \theta_{\min}}. \quad (26)$$

For sequential fragmentation involving CO^{2+} , $F = 3.86$, meaning each event within $\theta_{CO,S} = [8^\circ, 45^\circ]$ creates, on average, 3.86 equivalent events outside this range.

For each equivalent event, we transform to the body fixed xyz coordinate system given by Eqs (14–16), where $\theta_{AB,C}$ is defined in the xy plane as shown in Fig. 11. Since $N(\theta_{AB,C})$ is uniform, we rotate each event to a new, randomly selected, $\theta'_{AB,C}$, given by

$$\theta'_{AB,C} \equiv r(180 + \theta_{\min} - \theta_{\max}) + \theta_{\max} \pmod{180}, \quad (27)$$

outside the $[\theta_{\min}, \theta_{\max}]$ region, shown in Fig. 11(b). In Eq. 27, r is a random number uniformly distributed between $[0, 1]$. This rotation is performed while maintaining $|p_{AB}|$ constant and preserving the conjugate momentum associated with the first step, i.e., $p_{AB,C}$. If done correctly, the distributions inside and outside the $[\theta_{\min}, \theta_{\max}]$ region should have the same average number of counts. The equivalent events maintain the statistical fluctuations of the original data set since they are generated using the data and are rotated randomly.

The new conjugate momentum describing the second fragmentation step is given by

$$p'_{AB} = |p_{AB}| (-\sin \theta'_{AB,C} \hat{x} + \cos \theta'_{AB,C} \hat{y}). \quad (28)$$

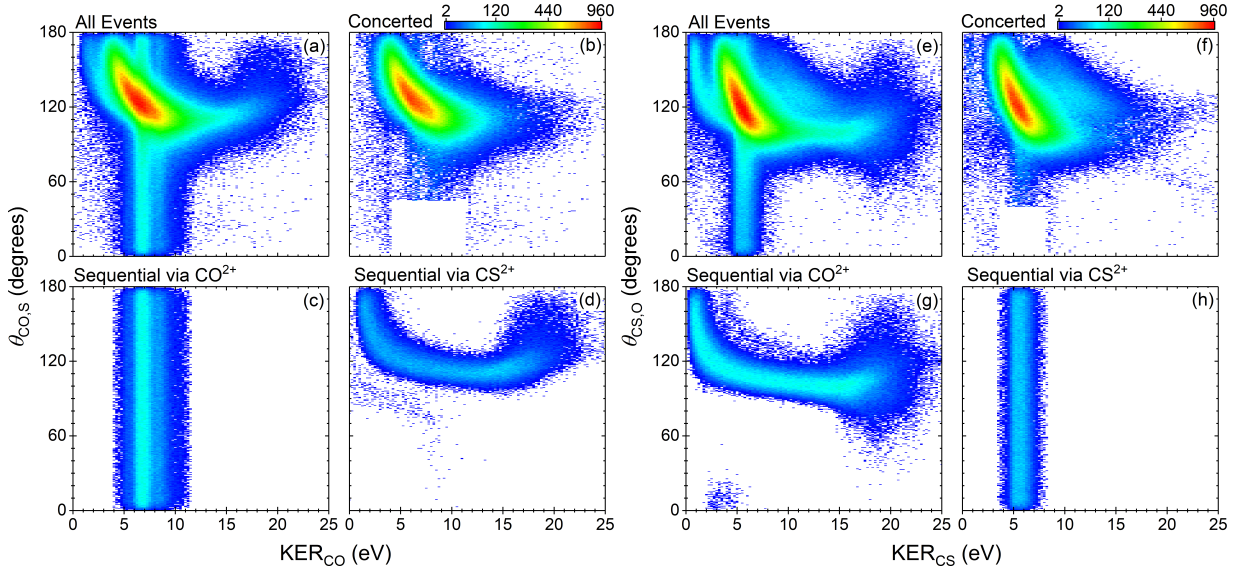


FIG. 12. (Color online) (a–d) The $N(\text{KER}_{\text{CO}}, \theta_{\text{CO,S}})$ distributions for (a) all $\text{O}^+ + \text{C}^+ + \text{S}^+$ events, (b) concerted fragmentation, and sequential fragmentation via (c) $\text{CO}^{2+} + \text{S}^+$ and (d) $\text{CS}^{2+} + \text{O}^+$. (e–h) Similar $N(\text{KER}_{\text{CS}}, \theta_{\text{CS,O}})$ distributions for (e) all events, (f) concerted fragmentation events, and sequential fragmentation via (g) $\text{CO}^{2+} + \text{S}^+$ and (h) $\text{CS}^{2+} + \text{O}^+$.

To determine the momenta of each individual fragment, we solve Eqs. (6, 8, 10) for $\mathbf{P}_A$, $\mathbf{P}_B$, and $\mathbf{P}_C$. With these momenta, we can determine the sequential fragmentation via $\text{AB} + \text{C}$ contributions in any plot.

The algorithm described above generates a uniform $N(\theta_{\text{AB,C}})$ distribution over all $\theta_{\text{AB,C}}$. However, our data contains ‘dips’ located at $\theta_{\text{CO,S}} = 0$ and 180° , as seen in Fig. 3(a-b). We explain the origin of these ‘dips’ in Appendix A using a simple model, which also indicates that the ‘dips’ are symmetric about $\theta_{\text{AB,C}} = 90^\circ$. To account for the ‘dips’, we modify our algorithm using a similar approach as detailed in Section IV C. Specifically, we select the data contained in the ‘dip’ on the edge where the sequential fragmentation events are clearly identified, given by the gate $[\theta_{\text{low}}, \theta_{\text{high}}] = [0, 8]$ for the CO^{2+} intermediate. Then we duplicate and rotate the events to $\theta'_{\text{CO,S}} = 180 - \theta_{\text{CO,S}}$ to preserve the shape of the dip. The reconstructed $N(\text{KER}_{\text{CO}}, \theta_{\text{CO,S}})$ distribution is shown in Fig. 10(c), while the resulting $N(\theta_{\text{CO,S}})$ distributions for each step of the reconstruction algorithm are detailed in Fig. 10(d).

The crux of this algorithm is that we retrieve the sequential fragmentation distribution, in regions obscured by other competing fragmentation mechanisms, exploiting the uniform $N(\theta_{\text{AB,C}})$ distribution. Since the algorithm works event-by-event and provides the momentum of each fragment, any plot can be created showing the contributions of each sequential fragmentation mechanism separately. It is important to note that the reconstruction algorithm only properly reproduces the distribution for states that have long enough lifetimes to create a uniform angular distribution.

In Section VI, we take the reconstruction algorithm presented above a step further and subtract the sequen-

tial fragmentation contributions from several plots containing all events, revealing the behavior of concerted breakup. To judge how well the reconstruction method works, we examine the quality of the subtractions to ensure no over-subtraction of the sequential breakup distributions occur, as shown in Appendix C.

VI. SEPARATING CONCERTED FROM SEQUENTIAL EVENTS: COMPARISON OF METHODS

In this section, we demonstrate the strength of applying the native-frames approach, where its extension allows us separate concerted from sequential fragmentation in any plot created from the measured momenta. In particular, we show how to properly subtract the sequential breakup contributions in the $N(\text{KER}_{\text{AB}}, \theta_{\text{AB,C}})$ plots, revealing the structures associated with concerted fragmentation. Additionally, we show that the reconstruction algorithm accurately reproduces the expected sequential fragmentation distributions in both Newton diagrams and Dalitz plots, and that sequential fragmentation via the $\text{SO}^{2+} + \text{C}^+$ is negligible under the conditions of our experiment.

A. Native-frames analysis with rotation in the fragmentation plane signature

In Fig. 12(a–d), we plot the $N(\text{KER}_{\text{CO}}, \theta_{\text{CO,S}})$ distribution and show the contributions of concerted breakup as well as sequential fragmentation involving the CO^{2+} and CS^{2+} intermediates. To determine the contribu-

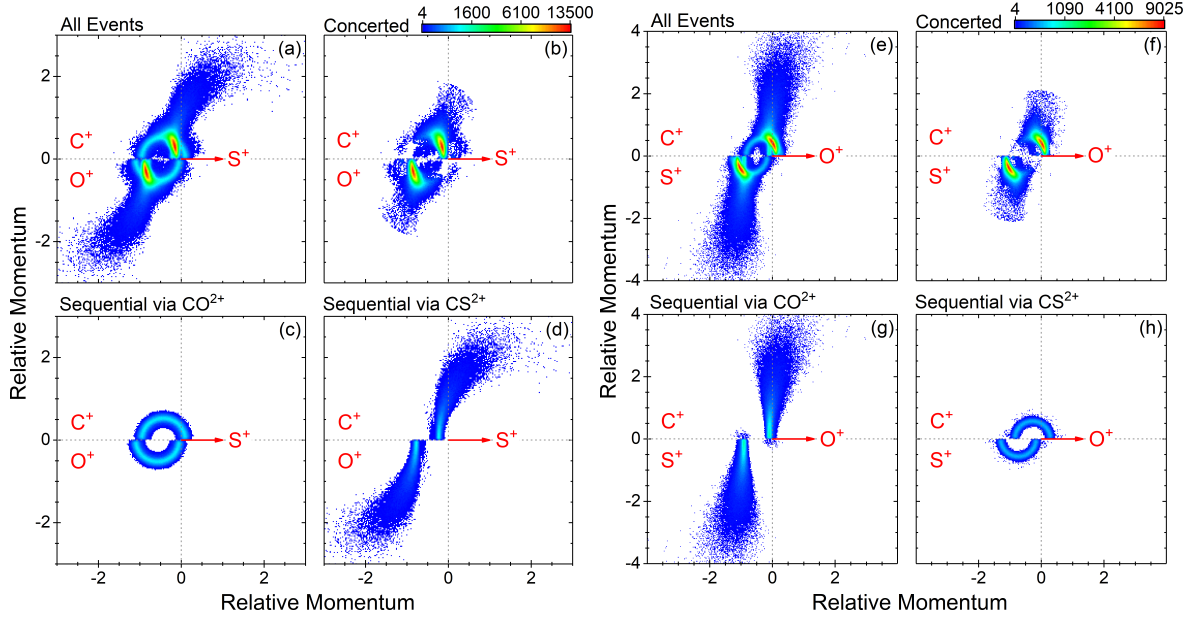


FIG. 13. (Color online) Newton diagrams with the S^+ momentum fixed along the x axis for (a) all $O^+ + C^+ + S^+$ events, (b) concerted fragmentation, and sequential fragmentation via (c) $CO^{2+} + S^+$ and (d) $CS^{2+} + O^+$. Similar Newton diagrams but with the O^+ momentum fixed along the x axis for (e) all $O^+ + C^+ + S^+$ events, (f) concerted fragmentation, and sequential fragmentation via (g) $CO^{2+} + S^+$ and (h) $CS^{2+} + O^+$.

tions of concerted fragmentation, shown in Fig. 12(b), the sequential breakup distributions in Fig. 12(c) and Fig. 12(d) are subtracted from the plot containing all events shown in Fig. 12(a). The analysis quantifying the quality of the resulting concerted breakup plot is discussed in Appendix C. The subtraction reveals that the large feature centered at $\theta_{CO,S} = 120^\circ$ is due to concerted breakup. Additionally, the feature extending over a wide KER_{CO} range arises from analyzing the sequential fragmentation via $CS^{2+} + O^+$ in the incorrect frame.

Note that the remaining density plots of the separated channels shown in this paper always follow the style of Fig. 12(a-d). Explicitly, the top left panel represents the entire data set, the top right panel contains the concerted breakup contributions while the bottom left and right show the sequential fragmentation distributions via the $CO^{2+} + S^+$ and $CS^{2+} + O^+$ channels, respectively.

Similarly, we plot in Fig. 12(e-h) the separated contributions of the concerted and sequential fragmentation distributions in the native frame associated with the CS^{2+} intermediate. Here too, the concerted breakup contributions appear as a feature centered at $\theta_{CS,O} = 120^\circ$ while the curved distribution originating at low KER_{CS} comes from the sequential fragmentation involving the CO^{2+} intermediate.

B. Newton diagrams

In a Newton diagram the sequential breakup is identified as a circular feature due to the rotation of the intermediate in the fragmentation plane [47]. To analyze

sequential fragmentation via the CO^{2+} intermediate, we choose to fix the momentum of the S^+ fragment along the x axis, while the C^+ and O^+ momenta are divided by $|\mathbf{p}_S|$ and placed in the upper and lower halves of the plot, respectively, as shown in Fig. 13(a). Figure 13(c) displays the expected offset semi-circle for sequential fragmentation via $CO^{2+} + S^+$. The ‘sprinkler’ shape extending to large relative momenta is due to sequential fragmentation involving the CS^{2+} molecule, as shown separately in Fig. 13(d). The concerted fragmentation contributions, shown in Fig. 13(b), demonstrate that the C^+ fragment tends to be ejected roughly perpendicular to the S^+ fragment while the O^+ is ejected at large angles with respect to the S^+ fragment.

Likewise, to analyze sequential fragmentation via the CS^{2+} intermediate, the O^+ momentum is chosen to be along the x axis of the Newton diagram while the C^+ and S^+ are scaled by $|\mathbf{p}_O|$ and placed in the upper and lower halves, respectively, as shown in Fig. 13(e). The CS^{2+} sequential channel also appears as an offset semi-circle, shown in Fig. 13(h). The other sequential channel involving the CO^{2+} intermediate emerges as a ‘sprinkler’-like feature in Fig. 13(g). The concerted fragmentation distribution, shown in Fig. 13(f), is similar to the results shown in Fig. 13(b).

C. Dalitz plots

As stated above, the Dalitz plot depicts energy sharing between the fragments [64]. In the case of OCS breaking into $O^+ + C^+ + S^+$, Wales *et al.* [52] identified the

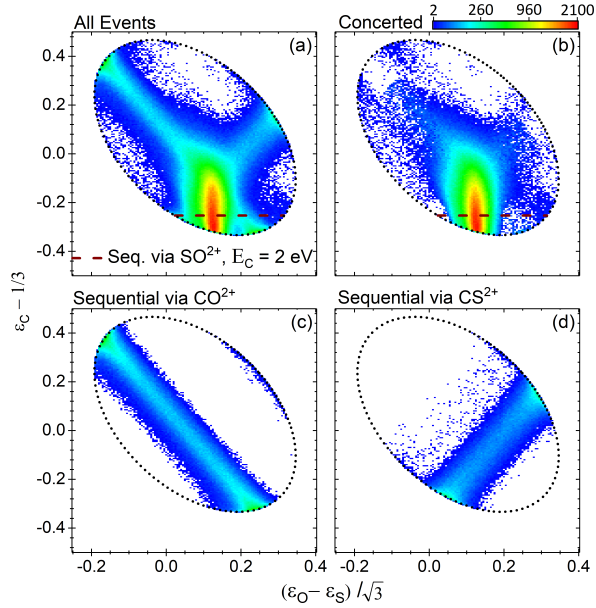


FIG. 14. (Color online) Dalitz plots for (a) all $\text{O}^+ + \text{C}^+ + \text{S}^+$ events, (b) concerted fragmentation, and sequential fragmentation via (c) $\text{CO}^{2+} + \text{S}^+$ and (d) $\text{CS}^{2+} + \text{O}^+$. The brown dashed line in panels (a-b) marks the expected location of sequential fragmentation via the SO^{2+} intermediate assuming $E_C = 2 \text{ eV}$ and a total KER of 20 eV (see Section VID).

features, in the Dalitz plot, associated with sequential fragmentation involving the CO^{2+} and CS^{2+} intermediate molecules. In this brief section, we show that the results of our analysis are consistent with their results.

We show the Dalitz plots of the separated concerted and sequential fragmentation distributions in Fig. 14, following the same choice of axes used by Wales *et al.* [52]. Recall that ε_i represents the scaled energy of fragment i , that is the kinetic energy of that fragment divided by the total kinetic energy release in the OCS^{3+} fragmentation. In particular, we observe straight line distributions due to the sequential fragmentation channels involving the CO^{2+} and CS^{2+} intermediate molecules, as shown in Fig. 14(c) and Fig. 14(d), respectively. The concerted distribution, which is a broad feature peaked at approximately $(x, y) = (0.125, -0.295)$ and extending to larger ε_C values, shows that the C^+ fragment accounts for a larger fraction of the total KER than expected for a linear geometry. This suggests that bending of the OCS molecule plays a role during concerted fragmentation.

D. Is there sequential fragmentation via $\text{SO}^{2+} + \text{C}^+$?

One would expect a low rate, if any, for sequential fragmentation of OCS^{3+} via $\text{SO}^{2+} + \text{C}^+$ since it requires bond formation between the two edge atoms. This less likely bond-rearrangement process has been observed in double ionization of some triatomic molecules [96–98].

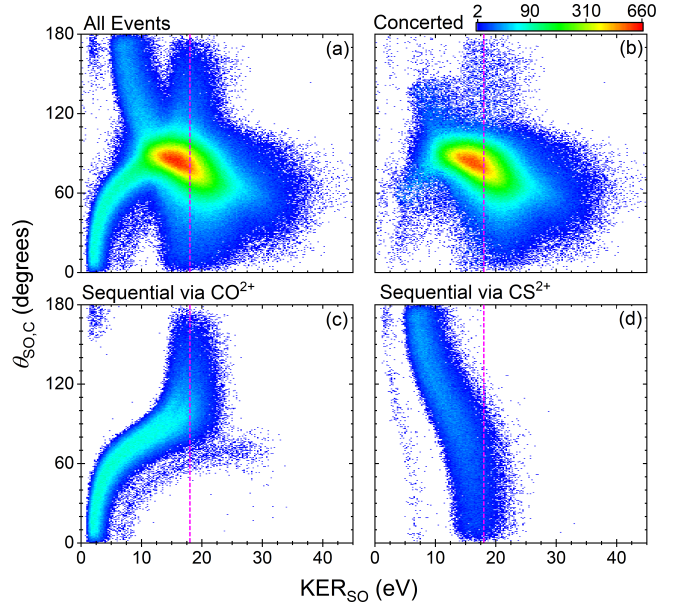


FIG. 15. (Color online) The $N(\text{KER}_{\text{SO}}, \theta_{\text{SO},\text{C}})$ distributions for (a) all $\text{O}^+ + \text{C}^+ + \text{S}^+$ events, (b) concerted fragmentation, and sequential fragmentation via (c) $\text{CO}^{2+} + \text{S}^+$ and (d) $\text{CS}^{2+} + \text{O}^+$. The magenta dotted lines at 18 eV indicate the apparent uniform $N(\theta_{\text{SO},\text{C}})$ distribution.

In this section, we implement the native-frames method to verify that this sequential channel is negligible in our experiment, while reviewing the method for identifying sequential fragmentation.

First, we plot the $N(\text{KER}_{\text{SO}}, \theta_{\text{SO},\text{C}})$ distributions in Fig. 15(a). An approximately uniform $N(\theta_{\text{SO},\text{C}})$ distribution centered around $\text{KER}_{\text{SO}} = 18 \text{ eV}$ in Fig. 15(a) suggests that sequential fragmentation via the SO^{2+} intermediate may be occurring. The KER_{SO} values are much higher than the $\lesssim 10 \text{ eV}$ expected for SO^{2+} [99], thus raising doubts if this sequential breakup truly occurs.

To further test if sequential fragmentation via the SO^{2+} intermediate occurs, we plot the $N(\gamma_{\text{SO}}, \theta_{\text{SO},\text{C}})$ distribution in Fig. 16(a). Recall that γ_{SO} is the Euler angle defined in Section IIIC. Figure 16(a) indicates that the uniform $N(\theta_{\text{SO},\text{C}})$ is not independent of the angle γ_{SO} , as expected for sequential fragmentation via $\text{SO}^{2+} + \text{C}^+$.

To determine the source of the uniform $N(\theta_{\text{SO},\text{C}})$ distribution visible in Fig. 15(a), we show the separated concerted- and sequential-fragmentation distributions in Fig. 15(b-d). These figures demonstrate that the uniform $N(\theta_{\text{SO},\text{C}})$ distribution, centered about 18 eV, is accidental, as it is due to a combination of sequential breakup via CO^{2+} and CS^{2+} , shown in Fig. 15(c-d), respectively. Note that part of this accidental uniform distribution is still visible in Fig. 15(b), which shows the concerted fragmentation after subtraction of the sequential-breakup channels shown in Fig. 15(c-d), however, this feature is on the level of the subtraction error.

Another indicator that the observed $N(\theta_{\text{SO},\text{C}})$ distribution is not due to sequential fragmentation via SO^{2+}

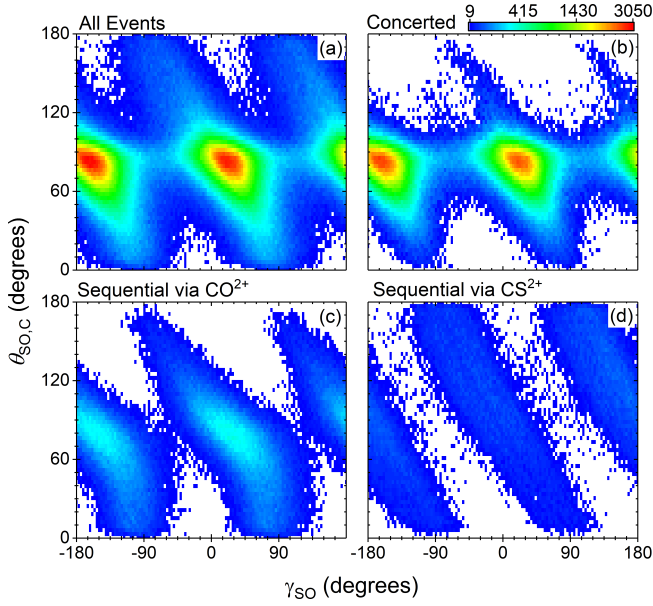


FIG. 16. (Color online) The $N(\gamma_{SO}, \theta_{SO,C})$ distributions for (a) all $O^+ + C^+ + S^+$ events, (b) concerted fragmentation, and sequential fragmentation via (c) $CO^{2+} + S^+$ and (d) $CS^{2+} + O^+$. Note that the $N(\gamma_{SO}, \theta_{SO,C})$ distributions for the sequential breakup via CO^{2+} and CS^{2+} are tilted (see text).

is provided by the channel separated $N(\gamma_{SO}, \theta_{SO,C})$ distributions are shown in Fig. 16. It is evident from this figure that the $N(\theta_{SO,C})$ distribution is not independent of γ_{SO} as it should for a SO^{2+} intermediate rotating in the fragmentation plane. The observed γ_{SO} dependence of the $N(\theta_{SO,C})$ distribution occurs because $\mathbf{p}_{SO,C}$ is not aligned along the projection of the polarization into the fragmentation plane, as is the case for the $\mathbf{p}_{CO,S}$ and $\mathbf{p}_{CS,O}$ conjugate momenta. Instead, it rotates in space since the $\mathbf{p}_{SO,C}$ momentum is related to the other sequential processes that exhibit the observe tilt when plotted versus γ_{SO} , as shown in Fig. 16(c-d).

Finally, if SO^{2+} is formed in the first fragmentation step, some of the metastable molecules should survive all the way to the detector, resulting in $SO^{2+} + C^+$ coincidence events. In our experiment, only 79 events passed the momentum conservation conditions for this channel, about the level of random-coincidence events. Moreover, if these are true events then the $SO^{2+} + C^+$ channel is about 7×10^{-4} times smaller than each of the other sequential breakup channels, i.e. $CO^{2+} + S^+$ and $CS^{2+} + O^+$. Though we cannot exclude sequential breakup via SO^{2+} completely, we can safely state that it has an extremely low rate in our experiment.

For comparison, we investigate whether or not Newton diagrams or Dalitz plots can better determine if this unlikely process occurs. To use the Newton diagram for identifying sequential fragmentation via the SO^{2+} intermediate, the C^+ momentum is set along the x axis while the O^+ and S^+ momenta are divided by $|\mathbf{P}_C|$ and plotted in the upper and lower halves of the figure, respectively.

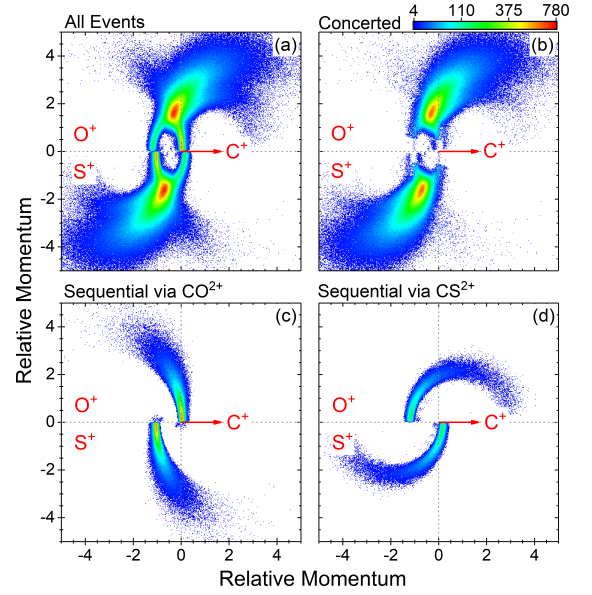


FIG. 17. (Color online) Newton diagrams with the C^+ fragment fixed to the x axis (see text) for (a) all $O^+ + C^+ + S^+$ events, (b) concerted fragmentation, and sequential fragmentation via (c) $CO^{2+} + S^+$ and (d) $CS^{2+} + O^+$.

The Newton diagram, shown in Fig. 17(a), exhibits a circular feature suggesting that sequential fragmentation via $SO^{2+} + C^+$ does occur. In reality, this feature is accidental, resulting from the other sequential fragmentation channels shown in Fig. 17(c-d), and vanishing upon their subtraction as demonstrated in Fig. 17(b).

Similarly, the Dalitz plot does not help identify if sequential fragmentation via $SO^{2+} + C^+$ occurs, but for a different reason. The distribution resulting from this sequential breakup should be centered around a constant ε_C because the energy of the C^+ , ejected during the first fragmentation step, is independent of the rotation of the SO^{2+} intermediate. Using the peaks of the measured total KER and KER_{SO} , the center of the distribution associated with the SO^{2+} intermediate in the Dalitz plot is predicted to be located around $(\varepsilon_C - 1/3) = -0.233$, marked by the brown dotted line in Fig. 14(a). This location is simulated assuming that $E_C = 2$ eV due to energy conservation and using the information that the total KER is centered at approximately 20 eV, as we show in Fig. 18. Based on the Dalitz plot, we cannot exclude the sequential channel involving the SO^{2+} intermediate until the other sequential channels are subtracted, as shown in Fig. 14(b). However, if the C^+ fragment acquired a larger fraction of the total KER than was assumed above, the Dalitz plot may facilitate the unique identification of sequential breakup via the SO^{2+} intermediate.

VII. A FORAY INTO SEPARATING CONCERTED FROM SEQUENTIAL FRAGMENTATION

In this section, we show additional specific examples, like the total KER, angular, and momentum distributions, where separating concerted from sequential breakup can help improve the interpretation of the data. However, since the reconstruction algorithm presented in Section V computes the three-dimensional momenta of the entire sequential fragmentation distribution, one is not limited to these few examples. Importantly, the method can be applied to any plot one can generate from the measured data.

A. Kinetic energy release

In Fig. 18, we plot the total KER for all three-body breakup into $O^+ + C^+ + S^+$ as well as the separated concerted and sequential breakup contributions. From this figure, we see that concerted fragmentation is shifted to higher KER as a result of the subtraction of the sequential breakup, which peaks a few eV lower. Assuming that all these fragmentation processes dissociate to the same, lowest, energy limit, this KER difference suggests that concerted fragmentation involves higher excited states of OCS^{3+} than the states leading to sequential breakup.

In addition, we plot the energy axis on the top of Fig. 18, which is identical to the axis in Fig. 7 and the potential energy plots shown in Ref. [87]. From this figure we see that concerted fragmentation peaks above 70 eV and extends from 64 to 90 eV. The lower limit suggests that the ground electronic state of OCS^{3+} does not contribute significantly to concerted breakup. Moreover, the Potential energy surfaces reported by Eland *et al.* [87] extend only up to 68 eV, while our data indicates the need to extend the structure calculation much higher in en-

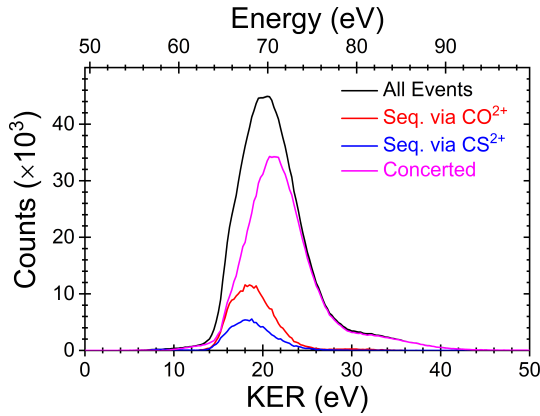


FIG. 18. (Color online) The separated $N(KER)$ distributions for sequential and concerted fragmentation. The top axis represents the energy of the transient OCS^{3+} relative to the $X^1\Sigma^+(v=0,0,0)$ ground state of the neutral OCS molecule.

ergy (i.e. by more than 20 eV) in order to identify the contributing states of the transient OCS^{3+} .

B. Angular distributions

Relative angular distributions following photofragmentation provide useful information about molecular breakup. In the case of sequential fragmentation, the axial recoil approximation breaks down and the resulting angular distributions change in ways that can be difficult to interpret. The reconstruction algorithm allows one to interpret the angular distributions by separating the sequential and concerted fragmentation distributions. In this section, we provide a few examples of how angular distributions, either relative within the molecular frame or with respect to lab-fixed coordinates, are altered by sequential fragmentation.

For the first example, we plot the separated sequential and concerted breakup contributions of the $N(\chi_C)$, $N(\chi_O)$, and $N(\chi_S)$ angular distributions in Fig. 19(b-d). The χ angles, illustrated in Fig. 19(a), are defined in the fragmentation plane described by the uvw coordinate system (see Appendix D for details). Briefly, χ_i is the angle between $\hat{u}$, representing the projection of the laser polarization into the fragmentation plane, and the momentum of each fragment, $\mathbf{P}_i$, where $i = C, O$, or S [cite papers using χ]. It is important to note that this coordinate system is similar to the body-fixed xyz coordinate system introduced in Section III D, except that the definition of $\hat{u}$ is fixed to the projection of the laser polarization while $\hat{y}$ is fixed to the first fragmentation step of sequential breakup.

In the case of the $N(\chi_O)$ distribution, shown in Fig. 19(c), the concerted breakup contributions peak at 0° and 180° , demonstrating that the O^+ fragment is ejected preferentially along the laser polarization. The sequential fragmentation channel via the CS^{2+} intermediate also displays similar behavior since the O^+ fragment is ejected during the first breakup step, which we have shown to be aligned along the polarization (see Section IV A). On the other hand, the $N(\chi_O)$ distribution for the sequential channel involving the CO^{2+} intermediate molecule is significantly flatter due to the rotation of the intermediate in the fragmentation plane. After subtracting the sequential contributions, we find that the full-width-half-maximum (FWHM) of the peaks at 0° and 180° shrinks to 80° for concerted fragmentation from 85° for all combined processes.

The separated $N(\chi_S)$ distributions are similar to the $N(\chi_O)$ distributions, except that the sequential breakup channels play opposite roles, as shown in Fig. 19(d). In particular, sequential fragmentation via the CO^{2+} intermediate is peaked along the laser polarization while the distribution for the CS^{2+} intermediate is significantly flatter. One difference between the concerted $N(\chi_S)$ and $N(\chi_O)$ distributions is that the FWHM of the peaks of the $N(\chi_S)$ distribution is 49° , significantly smaller than

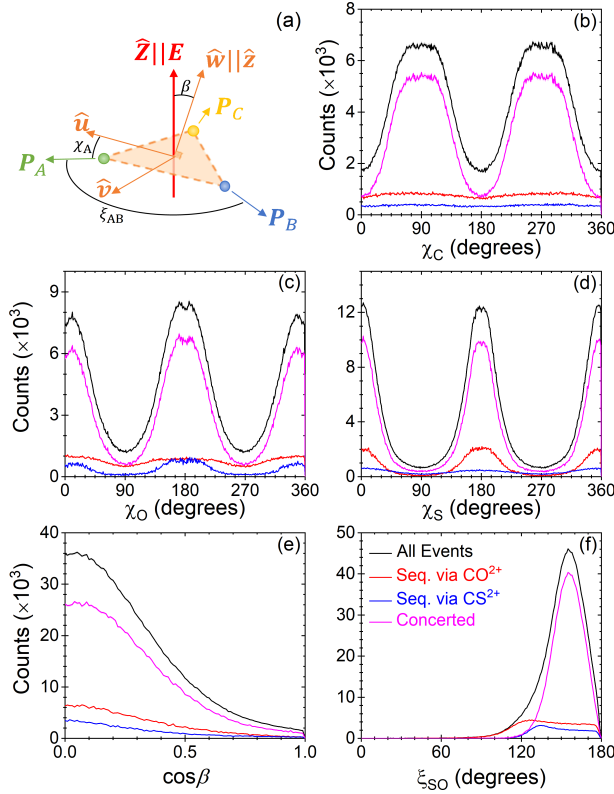


FIG. 19. (Color online) (a) A schematic of the uvw axes associated with the fragmentation plane and the angles β , χ_A and ξ_{AB} describing the fragmentation of an arbitrary ABC molecule into $A+B+C$. The (b) $N(\chi_C)$, (c) $N(\chi_O)$, (d) $N(\chi_S)$, (e) $N(\cos \beta)$, and (f) $N(\xi_{SO})$ angular distributions for the separated processes.

a FWHM of 80° for $N(\chi_O)$ — the reasons for this difference are not known yet.

In the case of the $N(\chi_C)$ angular distribution, shown in Fig. 19(b), the concerted breakup distribution is predominantly perpendicular to the laser polarization with a FWHM of 100° , significantly broader than the other two, $N(\chi_O)$ and $N(\chi_S)$, distributions. Additionally, both sequential breakup channels create flat distributions since the C^+ fragment undergoes rotation in both cases.

Recall that the angle between the polarization vector and the normal of the fragmentation plane, β , shown schematically in Fig. 19(a), is the Euler angle introduced in Sec. IIID and Fig. 5. To determine if the alignment of the fragmentation plane depends on the fragmentation process, we show the separated $N(\cos \beta)$ distributions in Fig. 19(e). Note that this plot is similar to the $\cos \beta_{AB}$ plots except for the fact $\cos \beta$ only spans from 0 to 1 due to the definition of $\hat{w}$. The $N(\cos \beta)$ distribution is peaked at $\cos \beta = 0$ for all processes, suggesting that fragmentation prefers that the polarization is mostly in the fragmentation plane. The distribution of the sequential and concerted breakup channels do not show a statistically significant difference.

The final plot Fig. 19(f) shows the angular distribu-

tion for the angle between the asymptotic momentum vectors of the S and O fragments, ξ_{SO} . The concerted breakup distribution peaks at 156° . The difference between the combined and concerted fragmentation distributions is that the FWHM of the $N(\xi_{SO})$ distribution changes from 32° to 28° , with a larger difference at smaller angles which are dominated by sequential fragmentation in the combined distribution. Sequential fragmentation, especially the channel involving the CO^{2+} intermediate, broadens the combined distribution due to the rotation of the intermediate molecule.

The angular distributions shown in this section are just a sample of the possible distributions that can be affected by sequential fragmentation. By applying the native-frames method and the sequential fragmentation signature to analyze the three-body fragmentation data, the different competing mechanisms can be separated, revealing the concerted fragmentation distribution and simplifying its interpretation.

C. Momentum distributions

Using the reconstruction algorithm, described in Sec. V, we determine the momenta of the generated equivalent events, thus allowing to plot separately the momentum distributions of sequential and concerted fragmentation. To demonstrate this point, we plot the separated fragmentation-plane momentum distributions of the C^+ and O^+ fragments in Figs. 20 and 21, respectively.

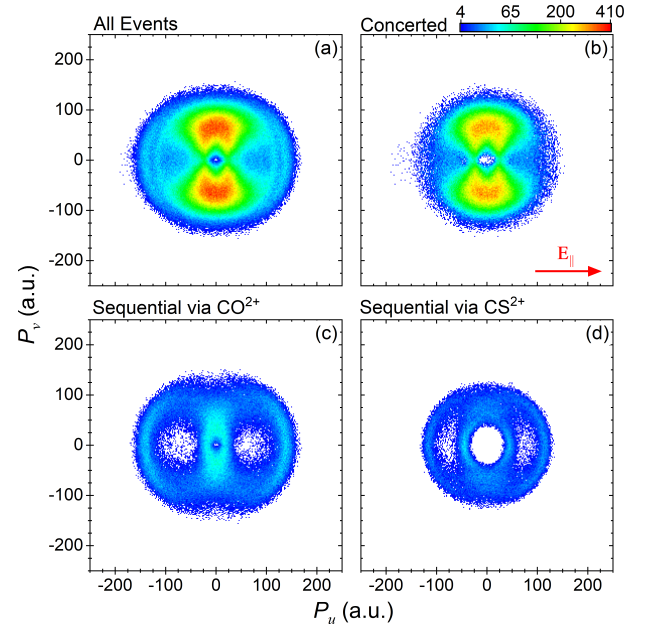


FIG. 20. (Color online) Momentum distributions of C^+ in the fragmentation plane for (a) all $O^+ + C^+ + S^+$ events, (b) concerted fragmentation, and sequential fragmentation via (c) $CO^{2+} + S^+$ and (d) $CS^{2+} + O^+$.

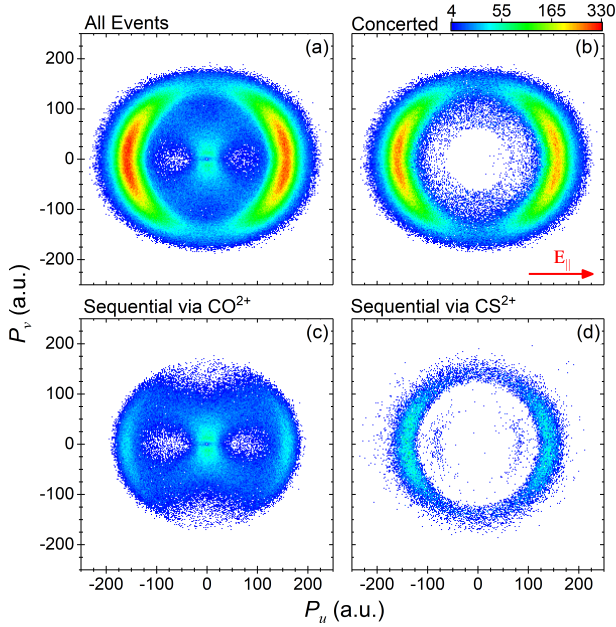


FIG. 21. (Color online) Momentum distributions of O^+ in the fragmentation plane for (a) all $O^+ + C^+ + S^+$ events, (b) concerted fragmentation, and sequential fragmentation via (c) $CO^{2+} + S^+$ and (d) $CS^{2+} + O^+$.

In the momentum distributions of the C^+ fragment shown in Fig. 20, both sequential fragmentation channels create offset circular distributions due to the rotation of the intermediate molecule in the fragmentation plane, consistent with what was shown in Fig. 19(b). Subtracting the sequential contributions yields the concerted distribution which is peaked perpendicular to the projection of the laser polarization into the fragmentation plane, denoted as $E_{||}$. Note that without the separation of sequential breakup contributions, the circular structures would have been difficult to interpret.

In Fig. 21, we show the momentum distributions of the O^+ fragment in the fragmentation plane. Here, the offset circular feature only appears in the momentum distribution for the sequential channel involving the intermediate CO^{2+} molecule, since it is the only sequential channel in which the O^+ fragment is involved in the rotation of the intermediate. In the sequential channel involving the CS^{2+} intermediate, the O^+ distribution remains aligned with the laser polarization, consistent with the alignment of the first fragmentation step, see Fig. 6. The momentum distribution of the S^+ fragment, not shown here, is similar to that of the O^+ fragment, except that the sequential channels play opposite roles as explained in the context of Fig. 19(d).

VIII. SUMMARY

This paper details the native-frames analysis method, which we apply to identify and separate sequential and

concerted fragmentation, as proposed in our previous publication [63]. Explicitly, the native frames analysis is based on the use of the conjugate momenta of the relevant Jacobi coordinates, i.e. the relative momenta. In addition, to identify the sequential breakup we use the rotation of the intermediate molecule in the fragmentation plane as the signature. This rotation results in a uniform $N(\theta_{AB,C})$ distribution. The advantage of our analysis is that it allows the separation of competing sequential and concerted fragmentation distributions, which may be vital for interpreting experiments. In addition, the method provides information about the sequential and concerted breakup mechanisms.

As the molecular imaging community moves toward measuring more complex molecules and higher-fold coincidence channels, researchers need to be mindful of possible contributions due to sequential fragmentation. In the case when polyatomic molecules are multiply ionized, the formation of metastable molecules with lifetimes of picoseconds or longer are likely to occur [100–102]. Therefore, sequential fragmentation can play a non-negligible role in the three- or more-body fragmentation, necessitating the ability to identify and separate its contributions from concerted fragmentation. Furthermore, the native-frames methodology can be methodically generalized to four- and more-body fragmentation channels using Jacobi coordinates, thus providing scientists with additional methods for visualizing their data, regardless if the molecule fragments through sequential or concerted breakup processes.

ACKNOWLEDGMENTS

This work is supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy under Award # DE-FG02-86ER13491.

Appendix A: Modeling $N(\theta_{AB,C})$ distribution

Throughout the paper, we surmised that the rotation of the AB intermediate molecule occurs in the fragmentation plane. As a result, even though $\theta_{AB,C}$ represents a polar angle in spherical coordinates, the signature of sequential fragmentation is a nearly uniform $N(\theta_{AB,C})$ distribution instead of a uniform $N(\cos\theta_{AB,C})$ distribution, which is the signature of an isotropic distribution as discussed in Section III C. We illustrate in Fig. 22 that the momentum, $\mathbf{p}_{AB}$, probability distribution is a ring produced by the rotation and breakup of the AB molecule in the fragmentation plane. The thickness of the ring is mainly attributed to the resolution of the measured momenta.

In this appendix, we explore the consequences of describing the ring distribution as a function of the spherical polar angle θ , which is equivalent to the angle $\theta_{AB,C}$

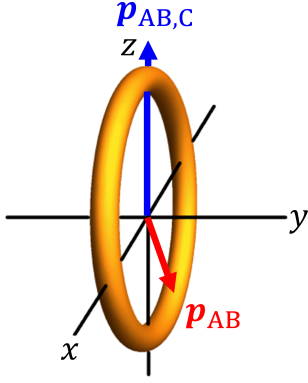


FIG. 22. (Color online) The isosurface of the $\mathbf{p}_{AB}$ probability distribution given by Eq. A1. Specifically, the surface is for a constant value of $\Phi = 0.5$, where $\Delta = 0.5$ and $\rho_0 = 4$.

between the two conjugate momenta. Specifically, we demonstrate that the thickness of this thin ring leads to ‘dips’ at the edges of the $N(\theta_{AB,C})$ distributions, similar to what we observe experimentally.

The ring distribution, shown in Fig. 22, is modeled using Gaussian distributions and is explicitly written as

$$\Phi(x, y, z) \propto \exp \left[-\frac{1}{2} \left(\frac{\rho - \rho_0}{\Delta} \right)^2 \right] \exp \left[-\frac{1}{2} \left(\frac{y}{\Delta} \right)^2 \right], \quad (\text{A1})$$

where ρ_0 is the radius of the ring in the XZ plane, Δ is the width in each direction, and ρ is given by

$$\rho = \sqrt{x^2 + z^2}. \quad (\text{A2})$$

Note that we set the width of the ring to be the same in both directions, which simplifies the following math significantly. Converting the expression to spherical coordinates gives

$$\Phi(r, \theta, \phi) \propto \exp \left[-\frac{1}{2} \left(\frac{r\chi - \rho_0}{\Delta} \right)^2 - \frac{1}{2} \left(\frac{r^2(1 - \chi^2)}{\Delta} \right)^2 \right], \quad (\text{A3})$$

with

$$\chi \equiv \frac{\rho}{r} = \sqrt{1 - \sin^2 \theta \sin^2 \phi}, \quad (\text{A4})$$

where θ and ϕ are the standard polar and azimuthal angles in spherical coordinates.

To determine the expected angular distribution $N(\theta)$, we integrate the function Φ over the radial and azimuthal coordinates assuming that $\rho_0 \gg \Delta$, i.e., the distribution width is small compared to its centroid. This approximation makes possible the analytic result

$$\Phi(\theta) \propto e^{-\beta \eta} [(2 - \eta) I_0(\beta \eta) + \eta I_1(\beta \eta)], \quad (\text{A5})$$

where $I_n(\beta \eta)$ are the modified Bessel functions while η and β are defined by

$$\eta = \sin^2 \theta, \quad (\text{A6})$$

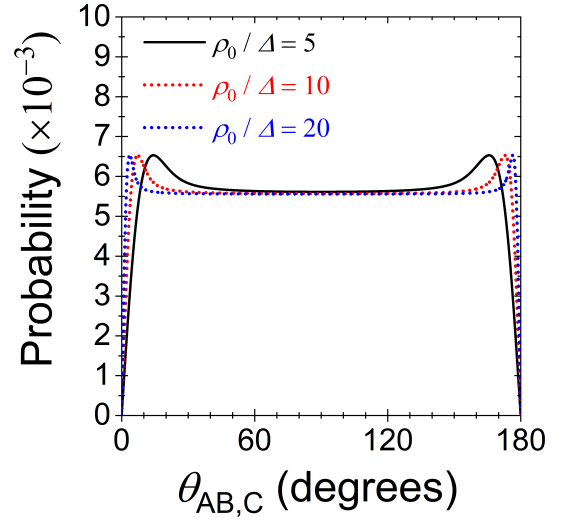


FIG. 23. (Color online) The normalized probability distribution $N(\theta) = \sin \theta \Phi(\theta)$ for $\rho_0/\Delta = 5, 10$, and 20 .

$$\beta = \frac{\rho_0^2}{2\Delta^2}. \quad (\text{A7})$$

We find that $\Phi(\theta)$ is symmetric about $\theta = \pi/2$ as one would expect.

Then, to plot the distribution of $N(\theta)$, we multiply $\Phi(\theta)$ by the volume element $\sin \theta$, resulting in the distribution shown in Fig. 23 for a few values of ρ_0/Δ . Note that the distribution shown is normalized, i.e., $\int_0^\pi N(\theta) d\theta = 1$, and it is plotted as a function of $\theta_{AB,C}$, which as stated above is the same as θ .

This model reproduces the ‘dips’ at the edges of the distribution. Furthermore, we see small peaks next to the ‘dips’ that we do not observe experimentally, most likely because of the reduced detection efficiency around the detector center, which affects mainly events with $\theta_{AB,C}$ as we discussed in Section III C.

It is important to mention that we do not need to incorporate the volume element, $\sin \theta$, in our experimental data because it is naturally accounted for when binning the data.

Appendix B: Classical model — dipole–point charge interaction

In this appendix, we describe the classical model used to determine the angular momentum gained by a heteronuclear diatomic molecule interacting with a point charge. Specifically, we use the sequential fragmentation of OCS via the CO^{2+} intermediate as an example. In this case, the angular momentum gain is perpendicular to the molecular plane due to the interaction between the permanent dipole of CO^{2+} and the S^+ fragment ejected in the first step, which is treated as a point charge.

In Fig. 24 we show a diagram of the initial conditions immediately after the rapid triple ionization of

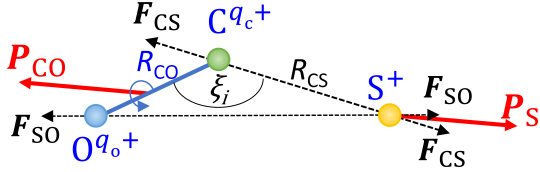


FIG. 24. (Color online) Schematic diagram of a bent OCS^{3+} leading to rotation of the CO^{2+} fragment (see text).

OCS , where we assume no stretching of the C–O and C–S bonds, i.e., equilibrium distances in the neutral OCS , given by $R_{\text{CO}} = 2.19$ and $R_{\text{CS}} = 2.95$ a.u., respectively [103]. On the other hand, the bond angle ξ_i , which is 180° for the equilibrium geometry of OCS , is used as a parameter. For the linear equilibrium configuration, the S^+ fragment does not apply any torque on the CO^{2+} fragment, hence the CO^{2+} molecule does not gain any angular momentum. In contrast, if the OCS molecule is bent, even slightly, the CO^{2+} does experience a torque and quickly gains significant angular momentum.

In order to compute the angular momentum gained by the CO^{2+} , we model it as a rigid rotor having two point charges, q_C and q_O , separated by R_{CO} . To evaluate the charges q_C and q_O , we use the calculated permanent dipole of the CO^{2+} ground electronic state at $R_{\text{CO}} = 2.19$ a.u., which is $D \simeq 3$ Debye [104] (with similar values for other low-lying states). For the origin defined at the CM of the CO^{2+} molecule, we approximate the dipole as

$$D = R_{\text{CO}} \left(\delta q + \frac{1}{7} \right), \quad (\text{B1})$$

where $q_C = 1 + \delta q \simeq 1.4$ and $q_O = 1 - \delta q \simeq 0.6$ a.u. Furthermore, we neglect the motion of the fragments associated with the molecule's initial vibration and rotation, which are expected to be very cold in the He seeded cold supersonic jet used in the experiment.

Due to the mutual Coulomb repulsion and conservation of linear momentum, the S^+ and CO^{2+} undergo back-to-

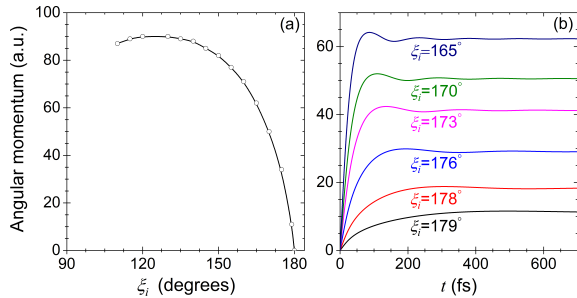


FIG. 25. (Color online) (a) Calculated final angular momentum of the CO^{2+} intermediate fragment of OCS as a function of the initial bond angle ξ_i . (b) The time evolution of the total angular momentum of the CO^{2+} for a few values of ξ_i . Note that angular momentum conservation holds for the whole $\text{S}^+ + \text{CO}^{2+}$ system.

back breakup. The translational and rotational motion is described by a set of coupled differential equations that we propagate in time (in steps of 1 a.u.). Specifically, we use the “ode45” function in MATLAB, which is based on the Runge-Kutta method, to solve the equations of motion numerically. We assume that the motion starts from rest at $t = 0$ a.u. at the internuclear distances associated with the equilibrium of the neutral molecule and neglect any initial angular momentum. The propagation of the equations of motion is terminated after 3×10^4 a.u. (i.e., about 725 fs) when the distance between the two fragments exceeds 350 a.u., at which time the CO^{2+} velocity and angular momentum converge to a constant value (smaller than 0.1 % deviations).

The calculated angular momentum of the intermediate CO^{2+} as a function of initial bond angle ξ_i is shown in Fig. 25(a). It can be clearly seen that the final angular momentum increases rapidly with bending of the OCS , resulting in a few tens of $\hbar$ for bending angles smaller than 177° . Moreover, the time evolution shown in Fig. 25(b) indicates that this angular momentum is gained in a couple hundred femtoseconds.

Appendix C: Quantifying the quality of the separated concerted breakup plots

In this Appendix, we discuss how to evaluate the quality of the subtractions leading to the separated concerted fragmentation plots. This analysis allows one to determine if the reconstruction algorithm accurately reproduces the sequential distributions by looking for over or under subtraction. As an example, we discuss the error in the concerted fragmentation $N(\text{KER}_{\text{CO}}, \theta_{\text{CO,S}})$ distribution. A similar analysis needs to be conducted for every concerted breakup plot to determine what features are statistically significant.

The separated concerted fragmentation plots are computed by subtracting the sequential fragmentation distributions from the distribution of all $\text{O}^+ + \text{C}^+ + \text{S}^+$ events. To quantify the error of the resulting concerted fragmentation distribution, statistical errors are propagated through the subtraction pixel-by-pixel to determine the error map.

In Fig. 26(a) and Fig. 26(b), the respective positive and negative values of the concerted fragmentation distributions are displayed. In particular, Fig. 26(b) shows that, in some regions, we over-subtract the sequential-breakup contributions. To determine if the over-subtraction is statistically significant, we divide, pixel-by-pixel, the yields N_{ij} by their error σ_{ij} , i.e. N_{ij}/σ_{ij} , as shown in Figs. 26(c) and Figs. 26(d) for positive and negative values, respectively. If $|N_{ij}/\sigma_{ij}| \leq 3$, the value of the pixel is consistent with zero, within the subtraction error. Since the majority of pixels in Fig. 26(d) are less than 2σ from zero, we conclude that the negative values resulting from the subtraction are within the statistical fluctuations of our data set.

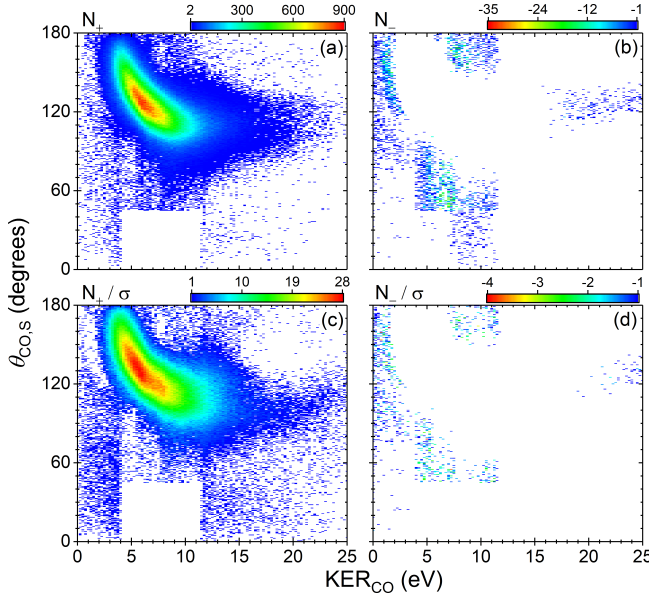


FIG. 26. (Color online) Characterization of the quality of the concerted fragmentation $N(\text{KER}_{\text{CO}}, \theta_{\text{CO},s})$ distribution. Plots of the (a) positive and (b) negative values of the $N(\text{KER}_{\text{CO}}, \theta_{\text{CO},s})$ distribution, and the similar (c) positive and (d) negative distributions determined by dividing the yields of each pixel N_{ij} by their error σ_{ij} .

Even though only the statistical analysis for the $N(\text{KER}_{\text{CO}}, \theta_{\text{CO},s})$ distribution is discussed in this Ap-

pendix, a similar analysis was conducted for every concerted breakup plot presented in this paper and in Ref. [63]. The quality of all the plots mentioned above are consistent with the example shown in this appendix.

Appendix D: Molecular fragmentation coordinate system definition

In Section VII B, we used a somewhat different coordinate system (specifically, the axes uvw shown in Fig. 19(a).) than the body-fixed fragmentation plane defined in Section III C.

The normal to the fragmentation plane $\hat{w}$ is equivalent to $\hat{z}$ given in Equation (14), except that $\hat{w}$ always points in the direction of the laser polarization $\hat{Z}$. This is accomplished by setting $\hat{w} = -\hat{z}$ whenever $\hat{z} \cdot \hat{Z} < 0$.

The $\hat{u}$ axis is defined as the projection of the polarization vector $\hat{Z}$ into the molecular plane,

$$\hat{u} = \frac{\hat{Z} - (\hat{Z} \cdot \hat{w}) \hat{w}}{|\hat{Z} - (\hat{Z} \cdot \hat{w}) \hat{w}|}, \quad (\text{D1})$$

and the remaining axis is

$$\hat{v} = \frac{\hat{w} \times \hat{u}}{|\hat{w} \times \hat{u}|}. \quad (\text{D2})$$

If needed, the momenta can be transformed to this coordinate system, as was done to produce Figs. 20 and 21.

-
- [1] B. Whitaker, ed., *Imaging in Molecular Dynamics - Technology and Applications* (Cambridge University Press, New York, NY, 2003).
 - [2] J. Ullrich, ed., *Ten years of COLTRIMS and Reaction Microscopes* (Max-Planck-Institut für Kernphysik Heidelberg, Heidelberg, Germany, 2004).
 - [3] G. E. Hall and P. L. Houston, *Annual Review of Physical Chemistry* **40**, 375 (1989), and references therein.
 - [4] Z. Vager, R. Naaman, and E. P. Kanter, *Science* **244**, 426 (1989).
 - [5] A. J. R. Heck and D. W. Chandler, *Annual Review of Physical Chemistry* **46**, 335 (1995), and references therein.
 - [6] J. Ullrich, R. Moshhammer, R. Dörner, O. Jagutzki, V. Mergel, H. Schmidt-Böcking, and L. Spielberger, *Journal of Physics B: Atomic, Molecular and Optical Physics* **30**, 2917 (1997).
 - [7] R. E. Continetti, *Annual Review of Physical Chemistry* **52**, 165 (2001).
 - [8] J. Ullrich, R. Moshhammer, A. Dorn, R. Dörner, L. P. H. Schmidt, and H. Schmidt-Böcking, *Reports on Progress in Physics* **66**, 1463 (2003).
 - [9] T. Weber, A. O. Czasch, O. Jagutzki, A. K. Müller, V. Mergel, A. Kheifets, E. Rotenberg, G. Meigs, M. H. Prior, S. Daveau, A. Landers, C. L. Cocke, T. Osipov, R. Díez Muiño, H. Schmidt-Böcking, and R. Dörner, *Nature* **431**, 437 (2004).
 - [10] D. Townsend, S. A. Lahankar, S. K. Lee, S. D. Chembreau, A. G. Suits, X. Zhang, J. Rheinecker, L. B. Harding, and J. M. Bowman, *Science* **306**, 1158 (2004).
 - [11] I. Ben-Itzhak, P. Q. Wang, J. F. Xia, A. M. Sayler, M. A. Smith, K. D. Carnes, and B. D. Esry, *Phys. Rev. Lett.* **95**, 073002 (2005).
 - [12] D. Rolles, M. Braune, S. Cvejanović, O. Geßner, R. Hentges, S. Korica, B. Langer, T. Lischke, G. Prümper, A. Reinköster, J. Viehhaus, B. Zimmermann, V. McKoy, and U. Becker, *Nature* **437**, 711 (2005).
 - [13] M. F. Kling, C. Siedschlag, A. J. Verhoef, J. I. Khan, M. Schultze, T. Uphues, Y. Ni, M. Uiberacker, M. Drescher, F. Krausz, and M. J. J. Vrakking, *Science* **312**, 246 (2006).
 - [14] F. Martín, J. Fernández, T. Havermeier, L. Foucar, T. Weber, K. Kreidi, M. Schöffler, L. Schmidt, T. Jahnke, O. Jagutzki, A. Czasch, E. P. Benis, T. Osipov, A. L. Landers, A. Belkacem, M. H. Prior, H. Schmidt-Böcking, C. L. Cocke, and R. Dörner, *Science* **315**, 629 (2007).
 - [15] D. Akoury, K. Kreidi, T. Jahnke, T. Weber, A. Staudte, M. Schöffler, N. Neumann, J. Titze, L. P. H. Schmidt, A. Czasch, O. Jagutzki, R. A. C. Fraga, R. E. Grisenti, R. D. Muiño, N. A. Cherepkov, S. K. Semenov, P. Ranitovic, C. L. Cocke, T. Osipov, H. Adaniya, J. C. Thompson, M. H. Prior, A. Belkacem, A. L. Landers,

- H. Schmidt-Böcking, and R. Dörner, *Science* **318**, 949 (2007).
- [16] E. Garand, J. Zhou, D. E. Manolopoulos, M. H. Alexander, and D. M. Neumark, *Science* **319**, 72 (2008).
- [17] M. S. Schöffler, J. Titze, N. Petridis, T. Jahnke, K. Cole, L. P. H. Schmidt, A. Czasch, D. Akoury, O. Jagutzki, J. B. Williams, N. A. Cherepkov, S. K. Semenov, C. W. McCurdy, T. N. Rescigno, C. L. Cocke, T. Osipov, S. Lee, M. H. Prior, A. Belkacem, A. L. Landers, H. Schmidt-Böcking, T. Weber, and R. Dörner, *Science* **320**, 920 (2008).
- [18] J. D. Savee, V. A. Mozhayskiy, J. E. Mann, A. I. Krylov, and R. E. Continetti, *Science* **321**, 826 (2008).
- [19] A. S. Sandhu, E. Gagnon, R. Santra, V. Sharma, W. Li, P. Ho, P. Ranitovic, C. L. Cocke, M. M. Murnane, and H. C. Kapteyn, *Science* **322**, 1081 (2008).
- [20] J. McKenna, A. M. Sayler, B. Gaire, N. G. Johnson, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Phys. Rev. Lett.* **103**, 103004 (2009).
- [21] G. Sansone, F. Kelkensberg, J. F. Pérez-Torres, F. Morales, M. F. Kling, W. Siu, O. Ghafur, P. Johnsson, M. Swoboda, E. Benedetti, F. Ferrari, F. Lépine, J. L. Sanz-Vicario, S. Zherebtsov, I. Znakovskaya, A. L'Huillier, M. Y. Ivanov, M. Nisoli, F. Martin, and M. J. J. Vrakking, *Nature* **465**, 763 (2010).
- [22] M. P. Grubb, M. L. Warter, H. Xiao, S. Maeda, K. Morokuma, and S. W. North, *Science* **335**, 1075 (2012).
- [23] M. Pitzer, M. Kunitski, A. S. Johnson, T. Jahnke, H. Sann, F. Sturm, L. P. H. Schmidt, H. Schmidt-Böcking, R. Dörner, J. Stohner, J. Kiedrowski, M. Reggelin, S. Marquardt, A. Schießer, R. Berger, and M. S. Schöffler, *Science* **341**, 1096 (2013).
- [24] J. A. DeVine, M. L. Weichman, B. Laws, J. Chang, M. C. Babin, G. Balardi, C. Xie, C. L. Malbon, W. C. Lineberger, D. R. Yarkony, R. W. Field, S. T. Gibson, J. Ma, H. Guo, and D. M. Neumark, *Science* **358**, 336 (2017).
- [25] C. E. M. Strauss and P. L. Houston, *The Journal of Physical Chemistry* **94**, 8751 (1990), and references therein.
- [26] R. N. Zare, *The Journal of Chemical Physics* **47**, 204 (1967).
- [27] R. R. Lucchese, A. Lafosse, J. C. Brenot, P. M. Guyon, J. C. Houver, M. Lebech, G. Raseev, and D. Dowek, *Phys. Rev. A* **65**, 020702 (2002).
- [28] D. Dowek, M. Lebech, J. Houver, and R. Lucchese, *Journal of Electron Spectroscopy and Related Phenomena* **141**, 211 (2004), frontiers of Coincidence Experiments.
- [29] D. Toffoli, R. R. Lucchese, M. Lebech, J. C. Houver, and D. Dowek, *The Journal of Chemical Physics* **126**, 054307 (2007), and references therein.
- [30] R. Guillemin, P. Decleva, M. Stener, C. Bomme, T. Marin, L. Journal, T. Marchenko, R. K. Kushawaha, K. Jänkälä, N. Trcera, K. P. Bowen, D. W. Lindle, M. N. Piancastelli, and M. Simon, *Nature Communications* **6**, 6166 (2015).
- [31] R. N. Zare, *Molecular Photochemistry* **4**, 1 (1972).
- [32] T. P. Rakitzis and R. N. Zare, *The Journal of Chemical Physics* **110**, 3341 (1999).
- [33] A. Hishikawa, H. Hasegawa, and K. Yamanouchi, *Chemical Physics Letters* **361**, 245 (2002).
- [34] N. Ferreira, L. Sigaud, and E. C. Montenegro, *The Journal of Physical Chemistry A* **121**, 3234 (2017).
- [35] S. Pathak, R. Obaid, S. Bhattacharyya, J. Bürger, X. Li, J. Tross, T. Severt, B. Davis, R. C. Bilodeau, C. A. Trallero-Herrero, A. Rudenko, N. Berrah, and D. Rolles, *The Journal of Physical Chemistry Letters* **11**, 10205 (2020).
- [36] Z. L. Streeter, F. L. Yip, R. R. Lucchese, B. Gervais, T. N. Rescigno, and C. W. McCurdy, *Physical Review A* **98**, 053429 (2018).
- [37] D. Reedy, J. B. Williams, B. Gaire, A. Gatton, M. Weller, A. Menssen, T. Bauer, K. Henrichs, P. Burzynski, B. Berry, Z. L. Streeter, J. Sartor, I. Ben-Itzhak, T. Jahnke, R. Dörner, T. Weber, and A. L. Landers, *Physical Review A* **98**, 053430 (2018).
- [38] P. M. Kroger and S. J. Riley, *The Journal of Chemical Physics* **67**, 4483 (1977).
- [39] U. Werner, K. Beckord, J. Becker, and H. O. Lutz, *Phys. Rev. Lett.* **74**, 1962 (1995).
- [40] C. Maul and K.-H. Gericke, *International Reviews in Physical Chemistry* **16**, 1 (1997), and references therein.
- [41] S. Hsieh and J. H. D. Eland, *Journal of Physics B: Atomic, Molecular and Optical Physics* **30**, 4515 (1997).
- [42] A. Hishikawa, H. Hasegawa, and K. Yamanouchi, *Chemical Physics Letters* **388**, 1 (2004).
- [43] A. Hishikawa, M. Ueyama, and K. Yamanouchi, *The Journal of Chemical Physics* **122**, 151104 (2005).
- [44] M. Ueyama, H. Hasegawa, A. Hishikawa, and K. Yamanouchi, *The Journal of Chemical Physics* **123**, 154305 (2005).
- [45] P. Liu, T. Okino, Y. Furukawa, T. Ichikawa, R. Itakura, K. Hoshina, K. Yamanouchi, and H. Nakano, *Chemical Physics Letters* **423**, 187 (2006).
- [46] A. Matsuda, M. Fushitani, R. D. Thomas, V. Zhaunerchyk, and A. Hishikawa, *The Journal of Physical Chemistry A* **113**, 2254 (2009).
- [47] N. Neumann, D. Hant, L. P. H. Schmidt, J. Titze, T. Jahnke, A. Czasch, M. S. Schöffler, K. Kreidi, O. Jagutzki, H. Schmidt-Böcking, and R. Dörner, *Phys. Rev. Lett.* **104**, 103201 (2010).
- [48] J. Wu, M. Kunitski, L. P. H. Schmidt, T. Jahnke, and R. Dörner, *The Journal of Chemical Physics* **137**, 104308 (2012).
- [49] L. Zhang, S. Roither, X. Xie, D. Kartashov, M. Schöffler, H. Xu, A. Iwasaki, S. Gräfe, T. Okino, K. Yamanouchi, A. Baltuska, and M. Kitzler, *Journal of Physics B: Atomic, Molecular and Optical Physics* **45**, 085603 (2012).
- [50] C. Wu, C. Wu, D. Song, H. Su, Y. Yang, Z. Wu, X. Liu, H. Liu, M. Li, Y. Deng, Y. Liu, L.-Y. Peng, H. Jiang, and Q. Gong, *Phys. Rev. Lett.* **110**, 103601 (2013).
- [51] R. Karimi, E. Bisson, B. Wales, S. Beaulieu, M. Giguère, Z. Long, W.-K. Liu, J.-C. Kieffer, F. Légaré, and J. Sanderson, *The Journal of Chemical Physics* **138**, 204311 (2013).
- [52] B. Wales, E. Bisson, R. Karimi, S. Beaulieu, A. Ramadnan, M. Giguère, Z. Long, W.-K. Liu, J.-C. Kieffer, F. Légaré, and J. Sanderson, *Journal of Electron Spectroscopy and Related Phenomena* **195**, 332 (2014).
- [53] A. Matsuda, E. J. Takahashi, and A. Hishikawa, *Journal of Electron Spectroscopy and Related Phenomena* **195**, 327 (2014).
- [54] A. Khan, L. C. Tribedi, and D. Misra, *Phys. Rev. A* **92**, 030701 (2015).
- [55] E. Wang, X. Shan, Z. Shen, M. Gong, Y. Tang, Y. Pan, K.-C. Lau, and X. Chen, *Phys. Rev. A* **91**, 052711 (2015).

- (2015).
- [56] S. Yan, X. L. Zhu, P. Zhang, X. Ma, W. T. Feng, Y. Gao, S. Xu, Q. S. Zhao, S. F. Zhang, D. L. Guo, D. M. Zhao, R. T. Zhang, Z. K. Huang, H. B. Wang, and X. J. Zhang, *Phys. Rev. A* **94**, 032708 (2016).
 - [57] A. Khan and D. Misra, *Journal of Physics B: Atomic, Molecular and Optical Physics* **49**, 055201 (2016).
 - [58] A. Ramadhan, B. Wales, R. Karimi, I. Gauthier, M. MacDonald, L. Zuin, and J. Sanderson, *Journal of Physics B: Atomic, Molecular and Optical Physics* **49**, 215602 (2016).
 - [59] Z. Shen, E. Wang, M. Gong, X. Shan, and X. Chen, *The Journal of Chemical Physics* **145**, 234303 (2016).
 - [60] U. Ablikim, C. Bomme, E. Savelyev, H. Xiong, R. Kushawaha, R. Boll, K. Amini, T. Osipov, D. Kilcoyne, A. Rudenko, N. Berrah, and D. Rolles, *Phys. Chem. Chem. Phys.* **19**, 13419 (2017).
 - [61] A. Khan, L. C. Tribedi, and D. Misra, *Phys. Rev. A* **96**, 012703 (2017).
 - [62] X. Ding, M. Haertelt, S. Schlauderer, M. S. Schuurman, A. Y. Naumov, D. M. Villeneuve, A. R. W. McKellar, P. B. Corkum, and A. Staudte, *Phys. Rev. Lett.* **118**, 153001 (2017).
 - [63] J. Rajput, T. Severt, B. Berry, B. Jochim, P. Feizollah, B. Kaderiya, M. Zohrabi, U. Ablikim, F. Ziaee, Kanaka Raju P., D. Rolles, A. Rudenko, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Phys. Rev. Lett.* **120**, 103001 (2018).
 - [64] R. Dalitz, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **44**, 1068 (1953).
 - [65] A. Abele *et al.*, *Physics Letters B* **469**, 270 (1999).
 - [66] R. Aaij *et al.*, *Physical Review D* **90**, 112004 (2014).
 - [67] B. Antolković and Z. Dolenec, *Nuclear Physics A* **237**, 235 (1975).
 - [68] R. Álvarez-Rodríguez, A. S. Jensen, E. Garrido, D. V. Fedorov, and H. O. U. Fynbo, *Physical Review C* **77**, 064305 (2008).
 - [69] K. Ogata, M. Kan, and M. Kamimura, *Progress of Theoretical Physics* **122**, 1055 (2009).
 - [70] O. S. Kirsebom, M. Alcorta, M. J. G. Borge, M. Cubero, C. A. Diget, R. Dominguez-Reyes, L. M. Fraile, B. R. Fulton, H. O. U. Fynbo, S. Hyldegaard, B. Jonson, M. Madurga, A. M. Martin, T. Nilsson, G. Nyman, A. Perea, K. Riisager, and O. Tengblad, *Physical Review C* **81**, 064313 (2010).
 - [71] J. Refsgaard, H. Fynbo, O. Kirsebom, and K. Riisager, *Physics Letters B* **779**, 414 (2018).
 - [72] R. Álvarez-Rodríguez, A. S. Jensen, E. Garrido, and D. V. Fedorov, *Physical Review C* **82**, 034001 (2010).
 - [73] C. Lin, *Physics Reports* **257**, 1 (1995).
 - [74] J. Z. H. Zhang, *Theory and Application of Quantum Molecular Dynamics* (WORLD SCIENTIFIC, 1998).
 - [75] P. Cornille, *Advanced Electromagnetism and Vacuum Physics* (WORLD SCIENTIFIC, 2003).
 - [76] D. J. Tannor, *Introduction to Quantum Mechanics: A Time-Dependent Perspective* (University Science Books, 2007).
 - [77] Y. Wang, Ph.D. thesis, Kansas State University (2010).
 - [78] V. L. B. de Jesus, B. Feuerstein, K. Zrost, D. Fischer, A. Rudenko, F. Afaneh, C. D. Schröter, R. Moshhammer, and J. Ullrich, *Journal of Physics B: Atomic, Molecular and Optical Physics* **37**, L161 (2004).
 - [79] Note that the A, B, and C labels represent atomic or molecular fragments, which may be neutral or charged.
 - [80] Note that a uniform $N(\cos\theta_{\text{CO,S}})$ distribution is proportional to $\sin\theta_{\text{CO,S}}$ when plotted in terms of $\theta_{\text{CO,S}}$.
 - [81] The uniform $N(\theta_{\text{CO,S}})$ distribution is proportional to $1/\sqrt{1 - \cos^2\theta_{\text{CO,S}}}$ when plotted in terms of $\cos\theta_{\text{CO,S}}$.
 - [82] J. P. Bouhnik, I. Gertner, B. Rosner, Z. Amitay, O. Heber, D. Zajfman, E. Y. Sidky, and I. Ben-Itzhak, *Phys. Rev. A* **63**, 032509 (2001).
 - [83] M. Lundqvist, P. Baltzer, D. Edvardsson, L. Karlsson, and B. Wannberg, *Phys. Rev. Lett.* **75**, 1058 (1995).
 - [84] M. Hochlaf, R. Hall, F. Penent, H. Kjeldsen, P. Lablanquie, M. Lavollée, and J. Eland, *Chemical Physics* **207**, 159 (1996).
 - [85] T. Šedivcová, V. Špirko, and J. Fišer, *J. Chem. Phys.* **125**, 164308 (2006).
 - [86] T. Šedivcová, P. R. Žd'ánská, V. Špirko, and J. Fišer, *The Journal of Chemical Physics* **124**, 214303 (2006).
 - [87] J. H. D. Eland, M. Hochlaf, P. Linusson, E. Andersson, L. Hedin, and R. Feifel, *The Journal of Chemical Physics* **132**, 014311 (2010).
 - [88] A. Kramida, Yu. Ralchenko, J. Reader, and NIST ASD Team, NIST Atomic Spectra Database (ver. 5.6.1), [Online]. Available: <https://physics.nist.gov/asd> [2019, February 4]. National Institute of Standards and Technology, Gaithersburg, MD. (2018).
 - [89] B. Darwent, *Bond dissociation energies in simple molecules*, NSRDS-NBS31 No. iv, 48 p. (U.S. National Bureau of Standards; for sale by the Supt. of Docs., U.S. Govt. Print. Off., [Washington], 1970) pp. iv, 48 p.
 - [90] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure— IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, 1979).
 - [91] G. Dawber, A. G. McConkey, L. Avaldi, M. A. MacDonald, G. C. King, and R. I. Hall, *Journal of Physics B: Atomic, Molecular and Optical Physics* **27**, 2191 (1994).
 - [92] E. Sidky and I. Ben-Itzhak, *Phys. Rev. A* **60**, 3586 (1999).
 - [93] L.-Y. C. Chiu, *The Journal of Chemical Physics* **40**, 2276 (1964).
 - [94] C. G. Stevens and J. C. D. Brand, *The Journal of Chemical Physics* **58**, 3324 (1973).
 - [95] For sequential fragmentation involving the CO^{2+} intermediate, the gated regions are $[\theta_{\min}, \theta_{\max}] = [8^\circ, 45^\circ]$ and $[\theta_{\text{low}}, \theta_{\text{high}}] = [0^\circ, 8^\circ]$. Similarly, the gates for sequential fragmentation involving the CS^{2+} intermediate are $[7^\circ, 40^\circ]$ and $[0^\circ, 7^\circ]$, respectively.
 - [96] S. Zhao, B. Jochim, P. Feizollah, J. Rajput, F. Ziaee, Kanaka Raju P., B. Kaderiya, K. Borne, Y. Malakar, B. Berry, J. Harrington, D. Rolles, A. Rudenko, K. D. Carnes, E. Wells, I. Ben-Itzhak, and T. Severt, *Phys. Rev. A* **99**, 053412 (2019).
 - [97] J. Laksman, D. Céolin, M. Gisselbrecht, and S. L. Sorensen, *The Journal of Chemical Physics* **133**, 144314 (2010).
 - [98] S. Larimian, S. Erattupuzha, S. Mai, P. Marquetand, L. González, A. Baltuška, M. Kitzler, and X. Xie, *Physical Review A* **95** (2017).
 - [99] A. B. Houria, Z. B. Lakhdar, M. Hochlaf, F. Kemp, and I. R. McNab, *The Journal of Chemical Physics* **122**, 054303 (2005).
 - [100] S. D. Price, *J. Chem. Soc., Faraday Trans.* **93**, 2451 (1997).

- [101] D. Schröder and H. Schwarz, [The Journal of Physical Chemistry A](#) **103**, 7385 (1999).
- [102] S. D. Price, [Phys. Chem. Chem. Phys.](#) **5**, 1717 (2003).
- [103] G. Herzberg, *Electronic spectra and electronic structure of polyatomic molecules* (Van Nostrand, 1966).
- [104] T. Šedivcová Uhlíková, P. R. Kaprálová-Žďáská, and V. Špirko, [International Journal of Quantum Chemistry](#) **107**, 2654 (2007).

3.5 Sequential fragmentation in the non-planar NH₃ molecule

This section contains our publication in the *Physical Review Research* journal. While this paper focuses on the general fragmentation dynamics of NH₃, where we measure two protons and two electrons following single-photon double ionization, I want to draw attention to Section IVB of the paper discussing sequential fragmentation, which is where I contributed most. The analysis and interpretation of the rest of the paper was lead by Kirk Larsen and Thomas Rescigno. Before continuing, it is important to note that since we only measure the two protons in coincidence, we calculate the final center-of-mass momentum of the unmeasured NH fragment and cannot tell if it broke. This detail becomes important later in our discussions of the paper.

Sequential fragmentation involving an NH₃ molecule adds some interesting complications that we did not encounter in the previous experiments. Recall from earlier, a necessary condition to generate a uniform angular distribution as a function of the angle between the conjugate momenta describing each step of sequential fragmentation, is that the rotation of the intermediate metastable molecule occurs in the fragmentation plane. However, because NH₃ is non-planar, this assumption does not hold, thus changing the signature of sequential fragmentation. Regardless of the breakdown of the assumption, we implemented the native frames approach, as shown in Fig. 3.3, and searched for a different signature to identify sequential breakup.

Specifically, we are analyzing sequential fragmentation occurring via



where H^+ and H^+ represent the protons emitted in the first and second step, respectively. We follow similar notation as described in Section 3.3, color coding the fragmentation path (i.e. ejection order) taken by the indistinguishable H^+ fragments. Furthermore, we plot

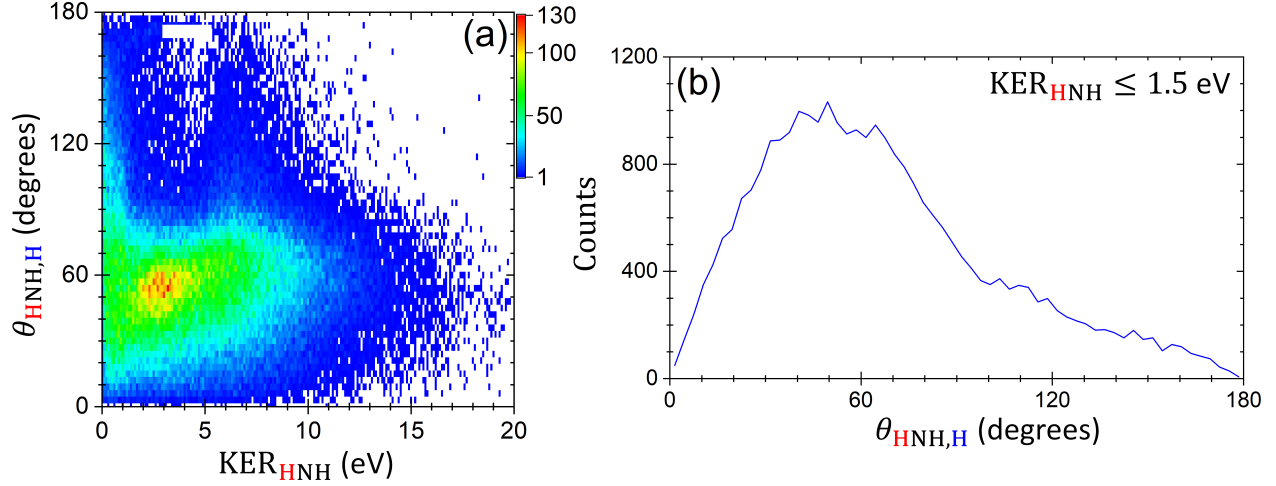


Figure 3.3: (a) The $N(\text{KER}_{\text{HNH}}, \theta_{\text{HNH,H}})$ distribution for NH_3^{2+} fragmentation into $\text{H}^+ + \text{H}^+ + \text{NH}$. (b) The $N(\theta_{\text{HNH,H}})$ distribution for events where $\text{KER}_{\text{HNH}} \leq 1.5 \text{ eV}$.

the $N(\text{KER}_{\text{HNH}}, \theta_{\text{HNH,H}})$ distribution in Fig. 3.3(a), meaning we are analyzing NH_3^{2+} fragmentation assuming it undergoes sequential fragmentation involving a NH_2^+ intermediate. Interestingly, this plot displays similar features to the sequential fragmentation contributions in D_2O , however, the angular distribution for events with $\text{KER}_{\text{HNH}} \leq 1.5 \text{ eV}$ is not uniform, as can be seen in Fig. 3.3(b). One of the reasons for this is due to the geometry of NH_3 , which leads to rotation of the NH_2^+ off the fragmentation plane. Furthermore, as we discuss in the paper, the likely sequential fragmentation pathway involves an NH^+ intermediate, not an NH_2^+ intermediate like assumed above. Unfortunately, since we only know the center-of-mass momentum of the unmeasured fragment, we cannot properly analyze the breakup into $\text{H}^+ + \text{H}^+ + \text{H} + \text{N}$. Therefore, to identify sequential fragmentation, we searched for a different signature.

The plot used to clearly identify sequential fragmentation is Fig. 5 in the following paper, which depicts the proton-proton energy correlation map for all $\text{H}^+ + \text{H}^+$ breakup events. In the case of the concerted fragmentation of NH_3 , both protons are ejected “simultaneously,” leading to equal energy sharing between them. On the other hand, sequential fragmentation appears as unequal energy sharing between the two protons, which is highlighted by magenta ovals in Fig. 5 of the paper. To understand why, we need to explain the step-by-step sequential fragmentation dynamics. Specifically, in the first step, the H^+ and NH^+ fragments

repel each other, leading to a large proton energy due to their Coulomb repulsion. Asymptotically, the NH^+ fragment is expected to be populated in its $X^2\Pi$ state, shown in Fig. 9 of the paper. In the second fragmentation step, the NH^+ dissociates into $\text{H}^+ + \text{N}$ due to the spin-orbit-coupling between the $X^2\Pi$ and $a^4\Sigma^-$ states. Note that only rovibrational states of $X^2\Pi$ above the $\text{H}^+ + \text{N}$ dissociation limit can fragment, providing an approximately 1 eV window of kinetic energy release. Thus, the H^+ fragments released in the second step have low kinetic energies and the two emitted protons have unequal energy sharing.

As stated above, my contributions to this project were in analyzing and understanding the sequential fragmentation dynamics. We chose not to include the native frames analysis presented above in this paper because the out-of-plane rotation and unmeasured fourth fragment added complications that we could not address without a more complete experiment in which both neutral fragments are also measured in coincidence. We plan to revisit the topic of “out-of-plane rotation” from similar trigonal pyramidal molecules, like H_3O^+ . Such an experiment is made possible using our recently upgraded ion-beam imaging method described in Section 2.5 where we can measure both neutral and ion fragments.

Photoelectron and fragmentation dynamics of the $\text{H}^+ + \text{H}^+$ dissociative channel in NH_3 following direct single-photon double ionization

Kirk A. Larsen,^{1,2,*} Thomas N. Rescigno,^{2,†} Travis Severt,³ Zachary L. Streeter,^{2,4} Wael Iskandar², Saijoscha Heck^{2,5,6}, Averell Gatton,^{2,7} Elio G. Champenois,^{1,2} Richard Strom,^{2,7} Bethany Jochim,³ Dylan Reedy,⁸ Demetri Call,⁸ Robert Moshhammer,⁵ Reinhard Dörner⁶, Allen L. Landers,⁷ Joshua B. Williams,⁸ C. William McCurdy,^{2,4} Robert R. Lucchese,² Itzik Ben-Itzhak³, Daniel S. Slaughter², and Thorsten Weber^{2,‡}

¹Graduate Group in Applied Science and Technology, University of California, Berkeley, California 94720, USA

²Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

³J. R. Macdonald Laboratory, Physics Department, Kansas State University, Manhattan, Kansas 66506, USA

⁴Department of Chemistry, University of California, Davis, California 95616, USA

⁵Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany

⁶J. W. Goethe Universität, Institut für Kernphysik, Max-von-Laue-Strasse 1, 60438 Frankfurt, Germany

⁷Department of Physics, Auburn University, Alabama 36849, USA

⁸Department of Physics, University of Nevada Reno, Reno, Nevada 89557, USA



(Received 29 June 2020; accepted 21 September 2020; published 9 October 2020)

We report measurements on the $\text{H}^+ + \text{H}^+$ fragmentation channel following direct single-photon double ionization of neutral NH_3 at 61.5 eV, where the two photoelectrons and two protons are measured in coincidence using three-dimensional (3D) momentum imaging. We identify four dication electronic states that contribute to $\text{H}^+ + \text{H}^+$ dissociation, based on our multireference configuration-interaction calculations of the dication potential energy surfaces. The extracted branching ratios between these four dication electronic states are presented. Of the four dication electronic states, three dissociate in a concerted process, while the fourth undergoes a sequential fragmentation mechanism. We find evidence that the neutral NH fragment or intermediate NH^+ ion is markedly rovibrationally excited. We also identify differences in the relative emission angle between the two photoelectrons as a function of their energy sharing for the four different dication states, which bare some similarities to previous observations made on atomic targets.

DOI: [10.1103/PhysRevResearch.2.043056](https://doi.org/10.1103/PhysRevResearch.2.043056)

I. INTRODUCTION

Photo-double-ionization (PDI) is a process in which two electrons are ejected from an atom or molecule by absorption of a single photon. The resulting dication can be produced through either an indirect or a direct process. In the indirect process [1,2], the target is first ionized to produce a photoelectron and a singly charged, excited cation. Subsequently, the cation decays by autoionization to produce a second continuum electron. The secondary electrons in indirect PDI have a unique signature, i.e., often a very narrow kinetic energy distribution and a rather isotropic angular emission pattern, which allows the process to be uniquely identified in a two-electron energy- or momentum-coincidence spectrum. In contrast to the indirect process, direct PDI involves simultaneous projection of two bound electrons to a correlated pair of

continuum states. The interaction of the two electrons makes PDI an ideal process for studying electron-electron correlation [3–7].

Because of the repulsive Coulomb interaction between singly charged ions that is active over very large internuclear distances, the vertical double-ionization thresholds of small molecules generally lie above the dissociation limits corresponding to the formation of singly charged fragments. Since the dissociative electronic states of a polyatomic dication can possess various fragmentation pathways involving different numbers of bodies, distinct fragment species can be measured depending on various factors. Studying the photoelectron pair and various ionic fragments in coincidence can provide information on electron-electron correlation, the features of dication potential energy surfaces, and the nuclear dynamics involved in the dication breakup. The molecular fragmentation that typically follows direct PDI can be broadly described as occurring in a single step (concerted), where all charged and neutral fragments are born simultaneously, or occurring in multiple steps (sequential), where first a portion of the charged and neutral fragments is generated, leading to a metastable intermediate moiety, which then undergoes further dissociation to produce the final set of fragments [8,9].

In sequential fragmentation, the decay of the metastable intermediate(s) can be facilitated by various mechanisms, such

*klarsen@lbl.gov

†tnrescigno@lbl.gov

‡tweber@lbl.gov

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](https://creativecommons.org/licenses/by/4.0/) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

as internal conversion or intersystem crossing to a dissociative state. Although spin-orbit coupling is generally weak in low- Z systems, intersystem crossing can in certain instances be the primary decay mechanism of metastable intermediates in a sequential dissociation process. Due to the weak coupling, the rate of intersystem crossing can be low, which leads to a significant period spent in the intermediate, providing time for the metastable fragments to rotate between the two fragmentation steps.

Distinguishing between concerted and sequential fragmentation channels is crucial in certain types of measurements, as concerted fragmentation channels can enable body-fixed frame photoelectron angular distributions to be retrieved, which carry far more information content than laboratory frame angular distributions. These body-fixed frame photoelectron angular distributions can, in most cases, only be reconstructed if the dication dissociates promptly along the relevant internuclear axes relative to rotation of those axes, allowing the molecular orientation at the instant of the PDI to be determined. This requirement is known as the axial recoil approximation [10]. Since measuring body-frame photoelectron angular distributions following PDI poses a great experimental challenge, there exists only a small body of literature covering this topic, primarily focused on H_2 [6,7,11–13]. Various experimental methods such as particle coincidence three-dimensional (3D) momentum imaging, including cold target recoil ion momentum spectroscopy (COLTRIMS), allow measurements to be made in the molecular frame, but they are predicated on the axial recoil approximation, hence it is useful to first determine which dication states exhibit concerted fragmentation mechanisms. The body-fixed frame electron emission pattern, or molecular frame photoelectron angular distributions (MFPADs), can be established if the complete structure of the molecule at the time of dissociation can be reconstructed from the detected heavy ionic fragments. However, if a dissociative channel produces more than two (undetected) neutral fragments, or results in a polyatomic fragment with unknown orientation, only the recoil frame photoelectron angular distribution (RFPAD) can be reconstructed. The latter represents the electron emission pattern with respect to a distinguished axis or plane spanned by the (detected) charged fragments. R/MFPADS are particularly sensitive to electron-electron correlation in both the initial and final states.

Various experimental and theoretical studies spanning a few decades have investigated the different dication electronic states and dissociation channels present in NH_3 following PDI, electron impact double ionization, and double ionization via double-charge-transfer spectroscopy [14–29]. Most of these studies have focused on determining the appearance energies of the different fragments and the energetic locations of the dication electronic states. Among these investigations, no study, to our knowledge, has examined the $H^+ + H^+$ fragmentation channels of ammonia.

In this work, we investigate $H^+ + H^+$ dissociation following direct valence PDI of neutral NH_3 at 61.5 eV, approximately 27 eV above the PDI threshold [17], where both the photoelectron and proton pairs are measured in coincidence using COLTRIMS. Based on multireference configuration-interaction (MRCI) calculations of dication po-

tential energy surfaces (PESs), we identify four dication electronic states that contribute to the $H^+ + H^+$ fragmentation. Our measurement provides the branching ratios between the four involved dication electronic states. As will be detailed below, of these four states, one appears to dissociate via a sequential mechanism and three dissociate in a concerted mechanism. Two of the three concerted dissociative states fragment at geometries near that of the ground state of neutral NH_3 , where the axial recoil approximation appears valid, while the third state undergoes a significant change in nuclear geometry prior to fragmentation. By measuring the correlated electron and ion fragment momenta, we determine that the neutral NH fragment or charged intermediate NH^+ cation is rovibrationally excited with considerable internal energy, in some cases more than 2 eV.

II. EXPERIMENT

The $H^+ + H^+$ fragmentation channel following valence PDI at 61.5 eV was investigated using COLTRIMS [30,31], where the two photoelectrons and two protons were collected with a full 4π solid angle, and their 3D momenta were measured in coincidence on an event-by-event basis. These four charged particles were guided using weak static parallel electric and magnetic fields, 11.4 V/cm and 10.0 G, respectively, to multihit position- and time-sensitive detectors at opposite ends of the spectrometer. Each detector comprised a multi-channel plate (MCP) stack in a chevron configuration for time readout, together with a delay-line anode, which decoded the hit position of each particle [32]. The electron and ion delay-line detectors were a hex-anode with an 80 mm MCP stack and a quad-anode with a 120 mm MCP stack, respectively. This system encodes a charge particle's 3D momentum into its hit position on the detector and time-of-flight (TOF) relative to each ionizing extreme ultraviolet (XUV) pulse emitted by the synchrotron. These detectors have a small but significant dead-time following each detected particle, therefore they are subject to limited multihit capability [32]. This problem is most prominent in the electron pair detection, due to the small differences in the electron arrival times and hit positions at the detector. This dead-time effect can influence measured relative electron-electron angular distributions and is thus important to quantify, in order to distinguish real features from those that may emerge due to the detection scheme. We point out that the photoions do not suffer from this dead-time problem to the same degree as the electrons, as they are much more spread out in TOF and hit position on the ion detector. The electron-pair resolution is estimated by simulating the charged particle motion in the spectrometer fields with various sum kinetic energies and in various energy-sharing conditions of the electron pair. For each pair of trajectories, the relative hit position and time-of-flight is computed, which is used to determine the fraction of simulated electron-pair events lost due to an estimated detector response, and thus approximate the fraction of actual losses.

The PDI experiment was performed using a tunable monochromatic linearly polarized beam of XUV photons produced at beamline 10.0.1.3. at the Advanced Light Source (ALS) synchrotron located at Lawrence Berkeley National Laboratory. The beamline monochromator was configured to

TABLE I. Ammonia dication vertical energies at neutral NH_3 geometry and asymptotic three-body limits extrapolated from *ab initio* calculations at $\text{N-H}_\text{I}/\text{N-H}_\text{II}$ distances of 50.0 bohr. Note that for the 1A_1 state (green), two possible asymptotic limits are given (see the text). Values in parentheses denoted by an asterisk are configuration-interaction results from Ref. [34].

State	Vertical energy (eV)	Asymptote	Adiabatic limit energy (eV)
$(1e^-)^3A_2$ (cyan)	8.64 (8.23)*	$\text{NH}(\tilde{^3}\Sigma^-)+\text{H}^++\text{H}^+$	0.96
$(1e^-)^1E$ (magenta)	9.94 (9.91)*	$\text{NH}^+(\tilde{^2}\Pi)+\text{H}+\text{H}^+$	0.52
$(1e^-)^1A_1$ (green)	11.94 (11.77)*	$\text{NH}(\tilde{^1}\Delta[\tilde{^1}\Sigma^+])+\text{H}^++\text{H}^+$	2.69 [3.74]
$(2a_1^{-1}, 3a_1^{-1})^1A_1$ (red)	18.94 (19.33)*	$\text{NH}(\tilde{^1}\Sigma^+)+\text{H}^++\text{H}^+$	3.74

provide 61.5 eV photons to the experiment, with an energy resolution narrower than ± 50 meV. The photon energy of 61.5 eV was chosen to be near the maximum of the PDI cross section of NH_3 , while at the same time providing electron kinetic energies that can be detected with full solid angle and adequate energy resolution (around 1:10). Moreover, it is beneficial to keep the electron sum energy greater than ~ 5 eV in order to utilize a large region of the 3D electron pair detection phase space, minimizing losses due to the electron detector dead-time (this will be apparent in Fig. 4 later in the discussion).

A beam of rotationally and vibrationally cold neutral NH_3 (~ 80 K) was produced by an adiabatic expansion of the pressurized target gas (~ 35 psi) through a $50\ \mu\text{m}$ nozzle, and collimated by a pair of downstream skimmers. The first skimmer has a diameter of 0.3 mm and the second skimmer has a diameter of 0.5 mm. The first skimmer is placed 8 mm downstream of the nozzle and in the zone of silence of the supersonic expansion. The second skimmer is 10 mm downstream of the first skimming stage. The resulting supersonic jet of target molecules propagated perpendicular to the photon beam, where the two beams crossed at the interaction region ($\sim 0.15 \times 0.15 \times 1.0\ \text{mm}^3$) inside the 3D momentum imaging spectrometer, where PDI of the neutral ammonia in its ground state occurs at an average rate of less than 0.01 events per XUV pulse, assuring unambiguous coincidence conditions.

The TOF and hit position of the charge particles produced by PDI were recorded in list mode on an event-by-event basis, enabling relevant events to be selected and examined in a detailed off-line analysis. For each PDI event, the kinetic energies and emission angles of the photoelectrons were determined from the 3D photoelectron momenta, while the orientation of the recoil frame and the kinetic energy release (KER) of the fragmentation were determined using the measured 3D momenta of the two protons. We infer the momentum of the center of mass of the remaining neutral NH radical by assuming momentum conservation between it and the two measured protons, treating the fragmentation as three-body breakup (even if the NH diatom fragments to $\text{N} + \text{H}$).

III. THEORY

Most previous work on the ammonia dication have been experimental in nature. Of the earlier theoretical studies, most have focused on computing the vertical double-ionization energy of neutral ammonia [17,33]. Tarantelli *et al.* [34] computed excited-state excitation energies of NH_3^{2+} at the equilibrium geometry of NH_3 (see also Table I), but to our

knowledge no earlier calculations of NH_3^{2+} potential surfaces have been reported. The electron configuration of NH_3 in its ground state is $(1a_1)^2(2a_1)^2(1e)^4(3a_1)^2$. At a photon energy of 61.5 eV, there are nine dication states that are energetically accessible following a vertical transition. To determine which of these states correlates with the three-body $\text{NH} + \text{H}^+ + \text{H}^+$ fragmentation channel, we carried out a series of electronic structure calculations. At each molecular geometry considered, we generated a set of molecular orbitals from a two-state, complete active space (CAS) multiconfiguration self-consistent field (MCSCF) calculation on the lowest triplet (3E) states of the dication. We kept one orbital ($\text{N}\ 1s$) frozen and included seven orbitals in the active space. We then performed MRCI calculations including all single and double excitations from the CAS reference space to generate 1D cuts through the PESs. All bond angles were frozen at the equilibrium geometry of neutral ammonia (107°), as was one hydrogen (H_{III}) bond length (1.9138 bohr), while two hydrogen bonds (H_I) and (H_II) were symmetrically stretched. The results of the calculations are shown in Fig. 1 with the electron configuration and state labels of each dication PES cut identified in the legend. The PES cuts were calculated out to a symmetric stretch $\text{N-H}_\text{I}/\text{N-H}_\text{II}$ distance of 50.0 bohr and extrapolated to infinity under the assumption of a purely repulsive Coulomb interaction between the positively charged fragments. The vertical energies at the neutral NH_3 geometry and the energies at the asymptotic limits are given in Table I. Note that here we do not explicitly consider cuts through the dication PESs where only one NH bond is stretched, as that is the subject of a future paper.

Our calculations reveal that there are only three three-body proton-proton dissociative limits. Of the three-body proton-proton channels, two are singlet states and one is a triplet state. The two singlet states leave the remaining neutral NH molecule in a $^1\Delta$ or a $^1\Sigma^+$ state, while the triplet leaves the neutral NH fragment in a $^3\Sigma^-$ state. To produce the two experimentally observed protons in the fragmentation, the implication is that an excitation must access one of these three dissociative limits, or undergo a four-body fragmentation mechanism that yields two protons, i.e., results in the fragments $\text{N} + \text{H} + \text{H}^+ + \text{H}^+$.

We identify three relevant singlet states, $(1e^-)^1E$, $(1e^-)^1A_1$, and $(2a_1^{-1}, 3a_1^{-1})^1A_1$, shown in Fig. 1(a) as solid curves (magenta, green, and red), and a fourth relevant triplet state, $(1e^-)^3A_2$, shown as a dashed curve (cyan). The curves in Fig. 1(a) are color-coded to be consistent with the experimental features to be discussed in the following section. Since spin-orbit coupling, required for an intersystem crossing, is

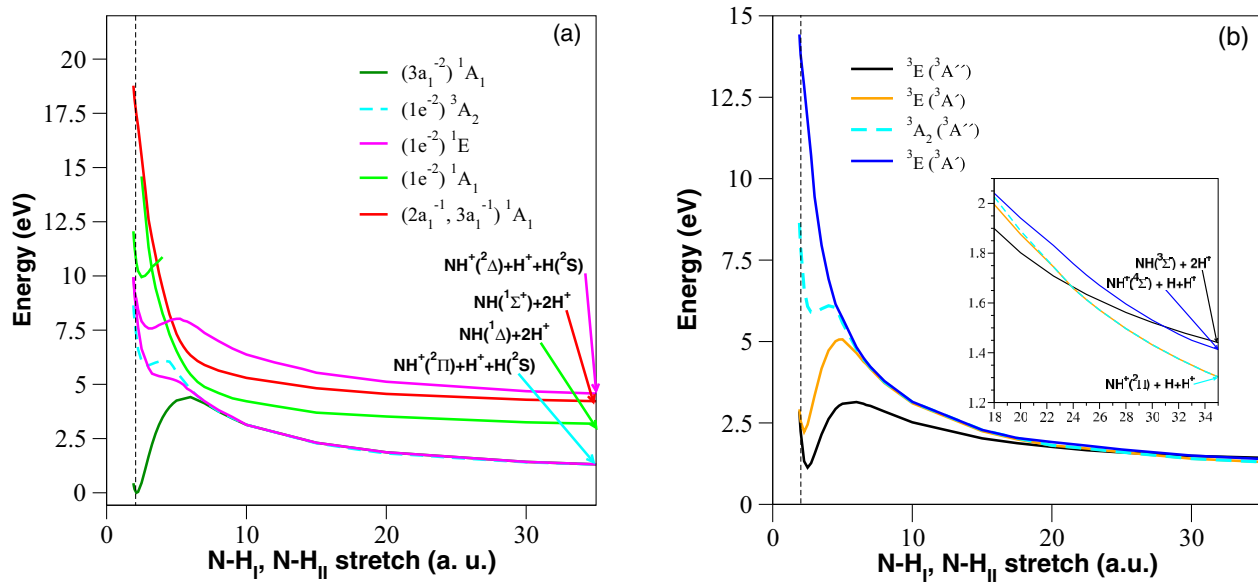


FIG. 1. PES cuts of the NH_3 dication generated from MRCI calculations as described in the text. Here, two protons are symmetrically stretched while the third remains fixed, with all internal angles frozen at the geometry of neutral ammonia. The zero of energy is set at the ground state (1A_1) of the ammonia dication at the geometry of neutral ammonia, which lies 34.8 eV below the dication [17]. On this energy scale, the 61.5 eV photon energy lies at 26.7 eV. The dashed vertical line indicates the equilibrium geometry of neutral ammonia. (a) Cuts of the experimentally identified relevant states; (b) detail of PES cuts for selected NH_3 dication triplet states. The inset indicates a region of large symmetric stretch distances where charge exchange may occur, as discussed in the text.

expected to be weak, the triplet state must dissociate to a triplet fragment state. However, Fig. 1 shows that the 3A_2 state (cyan dashed) actually correlates with the $\text{NH}^+(^2\Pi) + \text{H}^+ + \text{H}(^2S)$ dissociation channel [cyan dashed in the Fig. 1(b) inset]. To reach the $\text{NH}(^3\Sigma^-) + 2\text{H}^+$ limit (black curve in the inset) requires a charge exchange, which is possible at N-H separations greater than 18 bohr where the $^3E(^3A'')$ and $^3A_2(^3A'')$ states become nearly degenerate in energy across a range of geometries [see the cyan dashed and black curves in Fig. 1(b)]. This can result in charge exchange over a large range of distances along the asymmetric stretch coordinate that the dissociating wave packet traverses. We have observed an analogous asymptotic charge-exchange mechanism at such large N-H distances in an earlier study of dissociative electron attachment to ammonia [35].

For singlet states accessible in the Franck-Condon (FC) region as depicted in Fig. 1(a), there are two different proton-proton limits (red and green curves). The $(1e^{-2})^1A_1$ state (green) is seen to cross two other dissociative 1A_1 states (green and red), which correlate with the products $\text{NH}(^1\Delta)$ or $\text{NH}(^1\Sigma^+) + 2\text{H}^+$ plus two protons, respectively. Conical intersections (CIs) between the dissociative states and the initially excited 1A_1 state can result in dissociation to either of the singlet limits. Since the location of the CIs cannot be determined from 1D energy cuts (although numerous avoided crossing are observed), we must rely on the experimental findings to see which of the singlet limits are populated.

Previous experimental observations have indicated that PDI to the $(1e^{-2})^1E$ state is associated with the $\text{NH}^+ + \text{H}^+ + \text{H}$ fragmentation channel [15]. Since the dissociative limit of the $(1e^{-2})^1E$ state does not directly yield two protons, excitation to this state must undergo a nonadiabatic transition

to either of the two 1A_1 excited dication states, or the NH^+ fragment it produces must dissociate to $\text{N} + \text{H}^+$, in order to result in the measured two-proton coincidence.

The $(1e^{-2})^1E$ state, doubly degenerate in C_{3v} geometry, splits into A' and A'' states when two N-H bonds are symmetrically stretched. Of these two states, the upper state has A'' symmetry. Accordingly, internal conversion to either of the $^1A'$ states that have limits producing $\text{NH} + \text{H}^+ + \text{H}^+$ is unfavorable. Dissociation on the lower curve yields an NH^+ fragment in its $X^2\Pi$ ground state. If the NH^+ fragment is produced with sufficient internal energy, it can dissociate to $\text{N} + \text{H}(^2S)$ or through intersystem crossing to another NH^+ state, to $\text{N}(^4S) + \text{H}^+$. In the latter case this results in the production of two protons via a sequential four-body breakup $\text{NH}_3^{2+} \rightarrow \text{NH}^+ + \text{H}^+ + \text{H} \rightarrow \text{N} + 2\text{H}^+ + \text{H}$. This sequential breakup process will be examined in detail below.

IV. RESULTS AND DISCUSSION

Using the insights gained from the calculations on dication electronic states described in the previous section, we provide a detailed discussion of the experimental results in this section, which has been divided into three subsections. In the first subsection, we present and discuss the energetics of the photoelectrons and photoions, identifying features that correspond with the states outlined in the previous section. In the second subsection, we address the details of the dissociation dynamics by analyzing the relative emission angle between the two protons in each of these states. Lastly, we present results on the photoelectron dynamics via an analysis of the relative emission angle between the two photoelectrons for

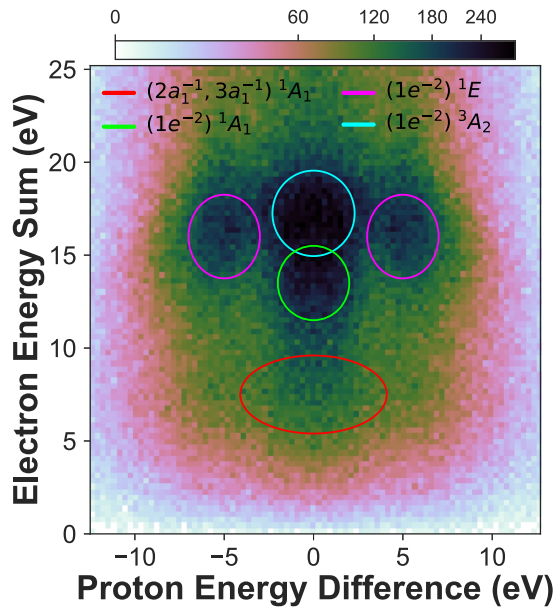


FIG. 2. The yield of $\text{H}^+ + \text{H}^+$ after valence PDI of NH_3 as a function of the energy difference of the proton pair and the energy sum of the photoelectron pair. The four color-coded ellipses guide the eye to the relevant features and dication states discussed in the text. The data have been mirrored about the zero proton energy difference, as there is no physical meaning to the order in which the two protons are detected.

the four dication states in different energy-sharing conditions of the electron pair.

A. Photoelectron and photoion energetics

The $\text{H}^+ + \text{H}^+$ fragmentation following PDI of NH_3 at 61.5 eV, ~ 27 eV above the PDI threshold, is identified and isolated by selecting the two charged fragments in the time-of-flight spectrum and then in momentum space, and by enforcing that two electrons are measured in coincidence with the two ionic fragments. First, we plot the PDI yield as a function of the energy difference between the two particles of the proton pair and the energy sum of the photoelectron pair. This plot is shown in Fig. 2.

Here we are able to identify four features, which we attribute to the four different dication electronic states calculated and tabulated in the previous section, resulting in photoelectron pairs with energy sums centered around 7.3, 14.1, 16.7, and 17.6 eV. These features are indicated by ellipses to guide the eye and color-coded to be consistent with the calculated values of 7.8, 14.8, 16.8, and 18.1 eV listed in Table I. The measured and calculated values are in excellent agreement and are consistent with the state assignments. Note that the ellipses do not reflect the actual software gates used in the data analysis. In the offline analysis, we choose each of these states by selecting carefully around the center of each feature in Fig. 2, while additionally placing constraints on the proton energy sum (which aids in separating the low and high KER features). Enforcing conditions in a multitude of dimensions in this fashion enables us to separate these four features for subsequent analysis.

Each of these four features possesses a full width at half-maximum (FWHM) in electron energy sum of roughly 6.2, 2.1, 4.2, and 2.4 eV, respectively. The FWHM of the electron energy sum of each dication state roughly indicates the magnitude of the gradient of the PES in the FC region, provided that the electron detector energy resolution is smaller than the width of the feature in question. To estimate the expected spread of observed photoelectron energies for the various dication states, we use a variant of the so-called reflection approximation [36]. The range of detectable KERs is determined by the FC envelope of the initial (neutral) vibrational state reflected onto the final dication PESs. We approximate the initial vibrational wave function with a harmonic-oscillator function χ_0 , obtained from a fit of the ground-state energy of ammonia as a function of the symmetric stretch coordinate. If we assume that the PDI cross section varies little over the FC region and that the final continuum vibrational wave functions can be approximated by δ functions about the classical turning points on the dication PESs [7], then the envelope of the expected photoelectron energies is given by the values of the vertical PDI energies as a function of the symmetric-stretch coordinate, weighted by the square of the symmetric-stretch vibrational wave function. We find that $|\chi_0|^2$ reaches half its maximum value at a symmetric-stretch displacement of approximately ± 0.11 Bohr from equilibrium, and we have used these values to calculate the FWHM of the photoelectron distributions. According to this procedure, we find widths of 5.1, 1.9, 3.1, and 2.2 eV, respectively, which are in good agreement with the measurement (see also Table II). From this we find that, given our photoelectron spectral resolution of roughly $\Delta E/E \sim 0.1$, the measured FWHM of each state does indeed roughly correspond with the gradient of its PES in the FC region.

We present the 1D photoelectron energy sum spectrum in Fig. 3, where each feature we identified in Fig. 2 has been indicated by the color-coded distribution. The peak value of each distribution has been indicated in Table II, where it is also compared with the theoretically calculated value. We find good agreement between the measurement and calculations. We can clearly identify the feature with a photoelectron energy sum centered near 7.3 eV, while the three higher photoelectron energy features appear clustered together. The branching ratios between the four measured features that correspond with the four dication states are estimated from the relative yield of these four features, and they are presented in Table III. The method for extracting these branching ratios is discussed later.

The yields of the $\text{H}^+ + \text{H}^+$ channels as a function of the kinetic energy of the first and second detected electron are plotted in the electron-electron energy correlation map shown in Fig. 4. Since the two electrons are indistinguishable particles, the labeling (as 1 and 2) is arbitrary and the figure has been symmetrized across the diagonal (the line $E_2 = E_1$) to account for this.

The four different features that correspond to the dication electronic states identified in Figs. 2 and 3 are indicated as color-coded diagonal lines (which take the form $E_2 = -E_1 + E_{\text{sum}}$, where E_{sum} is the photoelectron energy sum corresponding to that feature) in Fig. 4. We point out that the red diagonal line appears to be off the center of the diagonal feature, even

TABLE II. The measured and calculated photoelectron energy sum and KER centroids for each of the four identified features from $\text{H}^+ + \text{H}^+$ fragmentation following PDI of NH_3 at 61.5 eV. The asterisk marking the theoretical KER values indicates that these are calculated assuming ro-vibrational ground-state fragments, i.e., assuming maximum KER with no energy channeled into internal excitations. The theoretical KER values are all roughly 2 eV higher than the measured values, which is consistent with the dissociation producing fragments possessing approximately 2 eV of rovibrational energy (as explained in the text).

State	Photoelectron energy sum (eV)		KER (eV)	
	Experiment (FWHM)	Theory (FWHM)	Experiment (FWHM)	Theory* (FWHM)
$(1e^{-2})\ ^3A_2$ (cyan)	17.6 (2.4)	18.1 (2.2)	5.5 (2.0)	7.7 (2.2)
$(1e^{-2})\ ^1E$ (magenta)	16.7 (4.2)	16.8 (3.1)	7.7 (3.0)	9.4 (3.1)
$(1e^{-2})\ ^1A_1$ (green)	14.1 (2.1)	14.8 (1.9)	5.9 (2.2)	8.2 (1.9)
$(2a_1^{-1}, 3a_1^{-1})\ ^1A_1$ (red)	7.3 (6.2)	7.8 (5.1)	12.7 (6.1)	15.2 (5.1)

though this location represents the peak. This is because there are fewer bins along a given constant electron energy sum (i.e., a diagonal of the form $E_2 = -E_1 + E_{\text{sum}}$) as the photoelectron energy sum decreases. Since the length of a constant energy diagonal line scales as $\sqrt{2E_{e^-}}$, the number of available bins that events can populate decreases with decreasing E_{e^-} . This leads to the counts at low constant electron energy sums being concentrated in just a small number of bins, which can render the true location of the peak obscured in this 2D spectrum, while it is well represented in Fig. 3.

All four dication states are accessed via direct PDI, as indicated by the uniform diagonal features (taking the form $E_2 = -E_1 + E_{\text{sum}}$) and the absence of any Auger or autoionization lines, which would appear with vertical or horizontal characteristics at very unequal energy sharing due to the autoionization electron possessing a narrow constant (low)

energy. The uniformity of the diagonal features in Fig. 4 indicates that the two photoelectrons do not exhibit a strong preference toward either equal or unequal energy sharing, rather they exhibit roughly constant $\text{H}^+ + \text{H}^+$ yield as a function of the electron energy sharing (see also Fig. 12). The photoelectron energy-sharing distributions for each of the four states will be presented and discussed in more detail in the final Sec. IV C.

The same four features, corresponding with those seen in Fig. 2, are present in the proton-proton energy correlation map given in Fig. 5. As in the electron-electron energy correlation map of Fig. 4, the two protons are indistinguishable particles, hence the labeling is arbitrary and the figure has been symmetrized across the diagonal (the line $E_2 = E_1$). We have removed events that lie in the low-energy corner of Fig. 5, as the events that lie within this region originate from false coincidences. For each proton pair we compute the KER by treating the process as a three-body fragmentation and by inferring the momentum of the N-H center of mass via momentum conservation. Each feature seen in Fig. 5 possesses a different KER distribution centered around 12.7, 5.9, 7.7, and 5.5 eV, each with a FWHM of roughly 6.1, 2.2, 3.0, and 2.0 eV, respectively. These KER distributions are discussed in more detail later. The three KER features we have associated with the $(2a_1^{-1}, 3a_1^{-1})\ ^1A_1$, $(1e^{-2})\ ^1A_1$, and 3A_2 states exhibit a tendency toward equal energy sharing between the two protons, consistent with a concerted breakup mechanism. The fourth KER feature, associated with the 1E state, exhibits highly unequal energy sharing between the two protons, indicative of a sequential breakup mechanism.

Theoretical KER values are obtained by subtracting the asymptotic energies from the associated vertical PDI energies

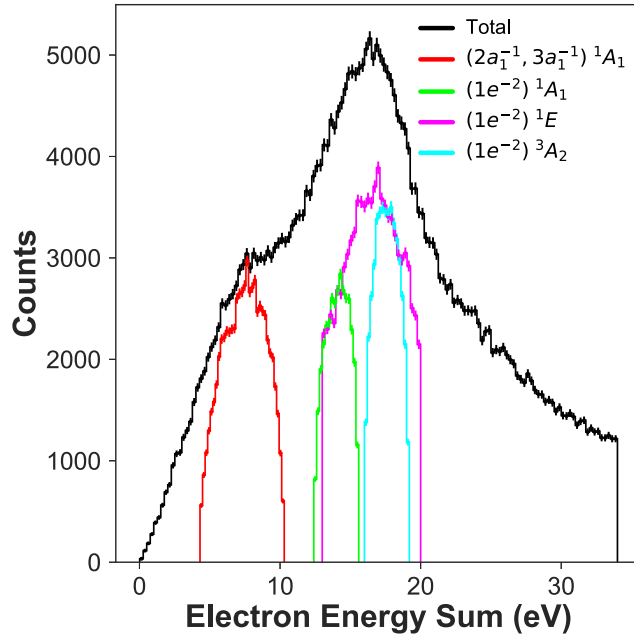


FIG. 3. The NH_3 PDI yield of the $\text{H}^+ + \text{H}^+$ channel as a function of the photoelectron energy sum integrated over all features (black) as well as for the four color-coded features corresponding to the identified dication states. The electron energy sum distributions for the four features have been scaled by a factor of 4, for better visibility.

TABLE III. The branching ratios for the four dication states contributing to the $\text{H}^+ + \text{H}^+$ dissociation channel following PDI of NH_3 at 61.5 eV. The errors on these fractions are estimated to be up to 5% (see text).

State	Branching ratio
$(2a_1^{-1}, 3a_1^{-1})\ ^1A_1$	14.6%
$(1e^{-2})\ ^1A_1$	4.5%
$(1e^{-2})\ ^1E$	18.1%
$(1e^{-2})\ ^3A_2$	62.8%

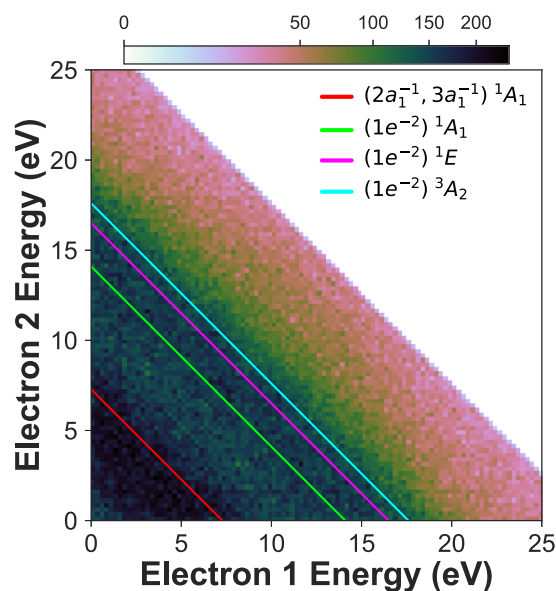


FIG. 4. Electron-electron energy correlation map for the $H^+ + H^+$ channels of the PDI of NH_3 . The four identified dication states are color-coded and indicated by diagonal lines.

in Table I, while theoretical photoelectron energy sum values are computed by subtracting these vertical PDI energies and the double ionization threshold from the photon energy. These results are displayed in Table II. For the concerted breakup channels, theory gives 15.2, 8.2, and 7.7 eV for the $(2a_1^{-1}, 3a_1^{-1})^1A_1$, $(1e^{-2})^1A_1$, and $(1e^{-2})^3A_2$ dication states, respectively. [Note that the $NH(^1\Sigma^+)$ asymptote has been used for both 1A_1 states.] These values are uniformly higher, by 2.5, 2.3, and 2.2 eV, respectively, than the measured val-

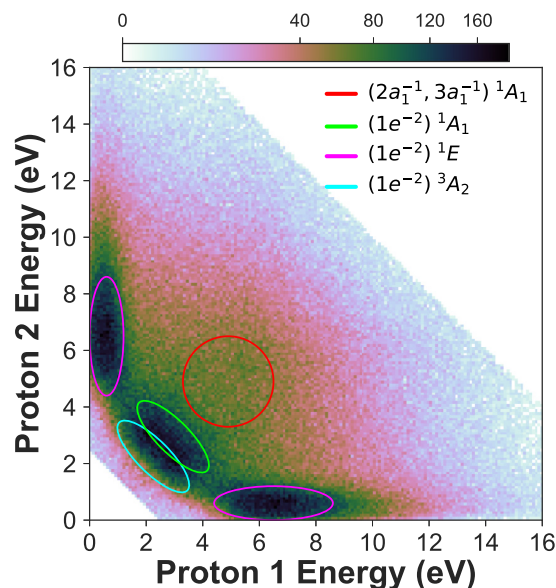


FIG. 5. Proton-proton energy correlation map for the $H^+ + H^+$ fragmentation channels of the valence PDI of NH_3 . The four identified dication states are color-coded and indicated by ellipses to guide the eye.

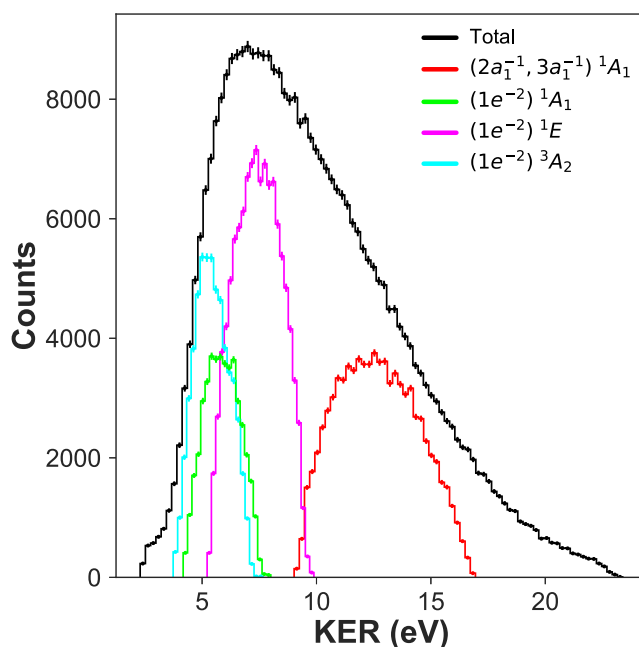


FIG. 6. The yield of $H^+ + H^+$ fragmentation channel of the valence PDI of NH_3 as a function of KER, shown for the total yield (black), as well as for the four color-coded features corresponding to the identified relevant dication states. The KER distributions for the four features have been scaled by a factor of 5 for better visibility.

ues. This discrepancy is either due to calculated dissociation energies that are all uniformly too small by approximately 2 eV, or it can arise if the NH fragment in all three concerted breakup channels is produced with approximately 2 eV of rovibrational energy. The energy balance of the sequential breakup is consistent with the high internal energy of the NH fragment. For the sequential 1E breakup channel, theory gives a KER value of 9.4 eV, which is 1.7 eV higher than the measured value. This corresponds to a four-body breakup mechanism, discussed in detail in Sec. IV B.

The FWHM of the KER distribution associated with each dication state carries similar information to the electron sum energy FWHM (see also Table II), indicating the steepness of the potential energy surfaces in the FC region, convoluted with the energy resolution of the ion spectrometer (estimated to be on the order of 100 meV). These values are indicated in Table II.

We show the 1D KER spectrum in Fig. 6, where each feature we identified in Fig. 5 has been indicated by the color-coded distribution. The peak value of each distribution is listed in Table II, where it is also compared with our theoretical results. The differences between the measured and calculated values in Table II are consistent with the molecular fragments containing roughly 2 eV of internal energy (or the aforementioned four-body breakup mechanism, which is discussed below) not explicitly accounted for in our theory, which only considers fragments in their rotational and vibrational ground states.

The estimated branching ratios between these four dication states are displayed in Table III. These branching ratios are approximated by simultaneously fitting each feature in Fig. 2

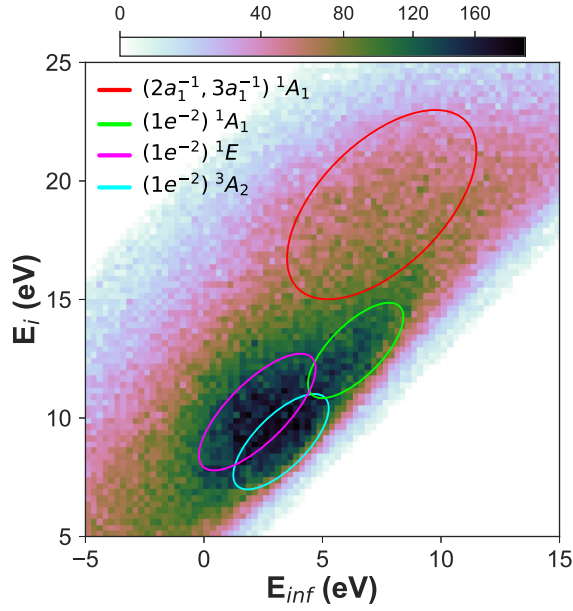


FIG. 7. The PDI yield of NH_3 at 61.5 eV as a function of the energy above the double-ionization threshold at the adiabatic limit following dissociation, E_{inf} , and the energy above the double-ionization threshold, E_i , for each of the four identified relevant dication states from the $\text{H}^+ + \text{H}^+$ fragmentation channel. The four identified dication states are color-coded and indicated by ellipses to guide the eye.

with a 2D Gaussian distribution (although the distributions may not be explicitly Gaussians, this is nonetheless a good approximation). The fitting procedure varied the widths along each dimension independently, while also including a varying constant background offset. Following this fitting procedure, we integrate the fit for each feature individually to estimate its contribution to the total $\text{H}^+ + \text{H}^+$ yield. The main contribution to the uncertainty of the branching ratio is rooted in the aforementioned electron pair deadtime, which influences the detection yield of the electron-ion coincidences for each dication state as a function of the electron sum energy. Applying the simulation mentioned above, we estimate the total possible loss in PDI yield for electron sum energies of 7.3 eV [$(2a_1^{-1}, 3a_1^{-1})^1A_1$], 14.1 eV [$(1e^{-2})^1A_1$], 16.7 eV [$(1e^{-2})^1E$], and 17.6 eV [$(1e^{-2})^3A_2$] to be 27.2%, 10%, 8.1%, and 7.5%, respectively. This translates to an error of up to 5% in the branching ratio. Errors due to deviations from the assumed Gaussian shape of each feature in the fitting process and the quality of the fit are estimated to be small ($<1\%$ and $<0.3\%$, respectively).

Lastly, we plot the $\text{H}^+ + \text{H}^+$ yield as a function of the energy at the adiabatic limit E_{inf} and the energy above the double ionization threshold E_i . This plot is shown in Fig. 7, with $E_i = \hbar\omega - \text{DIP} - (E_{e1} + E_{e2})$ and $E_{\text{inf}} = \hbar\omega - \text{DIP} - (E_{e1} + E_{e2} + \text{KER})$, where DIP is the double-ionization potential. As a guide to the eye, each of the four identified features have been indicated by ellipses. This plot indicates for each state and its dissociative limit where the NH_3^{2+} is excited to upon PDI, relative to the dication ground state. The circled features can be directly compared with the calculated vertical energy

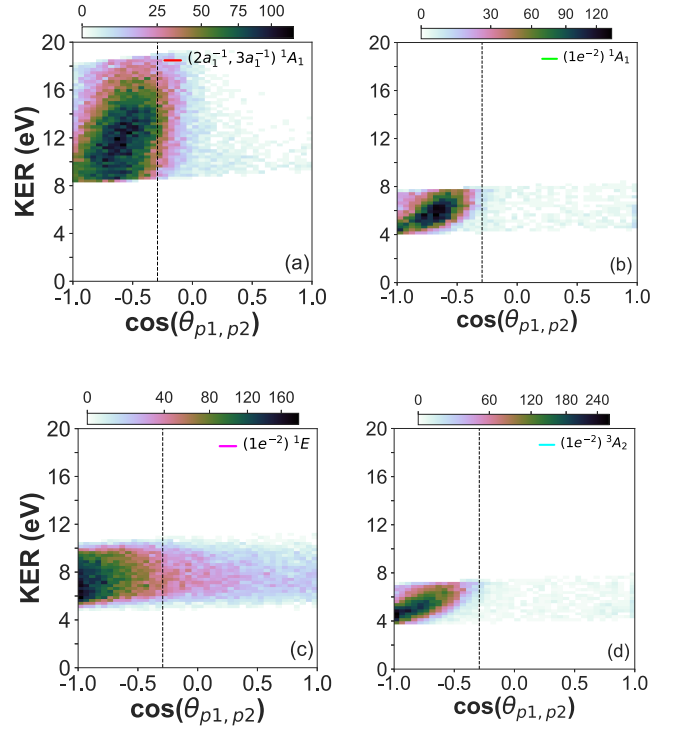


FIG. 8. The PDI yield of NH_3 as a function of cosine of the measured proton-proton angle, $\cos\theta_{p_1, p_2}$, and KER for each of the four dication states from the $\text{H}^+ + \text{H}^+$ fragmentation channel at 61.5 eV. The dashed black vertical line indicates the neutral ground state H-N-H angle.

and adiabatic energy values shown in Table I, which show good agreement with our theoretical results. As mentioned above, the measured energies E_{inf} are each approximately 2 eV higher than what is theoretically predicted for rotationally and vibrationally cold fragments, whereas the molecular fragments in the experiment can carry away this amount of energy internally, which we think is plausible from our analysis presented in Sec. IV B.

B. Photodissociation dynamics: Distinguishing concerted and sequential fragmentation

To examine the connection between the measured KER and the molecular geometry in each dication electronic state, we plot the yield as a function of cosine of the measured angle between the momenta of the two protons, $\cos\theta_{p_1, p_2} = \mathbf{p}_1 \cdot \mathbf{p}_2 / |\mathbf{p}_1||\mathbf{p}_2|$, and the KER, as shown in Fig. 8. It should be mentioned that due to the Coulomb repulsion between the two photoions, the measured proton-proton angle is an asymptotic dissociation angle, hence its value will be slightly larger than the true angle at which the fragmentation transpires. Although we do not have an exact estimate of how significantly the asymptotic dissociation angles differ from the true bond angles, our analysis carries useful information that differentiates the dissociation dynamics for each of the four features. In Fig. 8, the neutral ground-state geometry of NH_3 (specifically the H-N-H bond angle) is indicated by the vertical black dashed line. First, we point out that of the four dication states, three—the $(2a_1^{-1}3a_1^{-1})^1A_1$, $(1e^{-2})^1A_1$, and

($1e^{-2}$) 1A_1 states—exhibit decreasing KER with increasing measured dissociation angle between the protons, as seen in Fig. 8. Qualitatively, if the angle between the two protons increases due to nuclear motion in the dication, e.g., the NH_3 umbrella opening, their separation increases and their Coulomb repulsion correspondingly decreases, resulting in the negative bivariate correlation between the KER and the proton-proton angle, θ_{p_1,p_2} . Although this type of nuclear motion was not addressed in our calculations (which kept bond angles frozen), we still bring forward this qualitative picture as a possible explanation for the observed correlation. This also gives further support to the notion that these three dication states dissociate via a concerted mechanism, where the two protons are simultaneously eliminated from the dication.

We also point out that the features associated with the ($2a_1^{-1}, 3a_1^{-1}$) 1A_1 state and the ($1e^{-2}$) 1A_1 state dissociate at angles closer to the neutral ground-state geometry of the NH_3 molecule (H-N-H bond angle $\sim 107^\circ$) than the feature associated with the ($1e^{-2}$) 3A_2 state, which tends to fragment at angles approaching 180° . Although the distributions for the ($1e^{-2}$) 1A_1 and ($1e^{-2}$) 3A_2 states appear similar in shape, each state's fragmentation dynamics can be distinguished as different by the location of their respective peaks in the measured proton-proton angle. This suggests that the ($2a_1^{-1}, 3a_1^{-1}$) 1A_1 and the ($1e^{-2}$) 1A_1 states exhibit prompt fragmentation, while the molecular structure in the ($1e^{-2}$) 3A_2 state evolves further away from the neutral configuration, driven toward larger bond angles between the two protons, prior to dissociation. This is indeed consistent with the asymptotic charge exchange mechanism, described in Sec. III, that couples the 3A_2 ($^3A''$) and 3E ($^3A'$) states [PES cuts inset in Fig. 1(b)]. The dissociation on the ($2a_1^{-1}, 3a_1^{-1}$) 1A_1 and ($1e^{-2}$) 1A_1 states result in the direct elimination of two protons, which are light and depart fast, providing little time for the molecular structure to evolve away from the neutral equilibrium geometry during the fragmentation. In contrast, the fragmentation on the ($1e^{-2}$) 3A_2 state initially involves a heavier NH^+ ion preceding the charge exchange mechanism that produces a light proton. Thus the initial dissociation on the ($1e^{-2}$) 3A_2 state (prior to the charge exchange) is slower due to the increased mass of one of the charged fragments.

Although our calculations keep the bond angles frozen, it is known that for molecules of the form AH_3 , ionization from the $1e$ orbital [as in the case of the ($1e^{-2}$) 3A_2 state] drives the molecule toward a planar configuration, i.e., larger H-N-H bond angles (this can be seen in a Walsh diagram; see Ref. [37]). The increased fragmentation time leads to an increased likelihood for processes such as the aforementioned charge exchange to take place, as well as more time for the molecular geometry to evolve away from the neutral equilibrium geometry toward larger H-N-H angles, preceding the dissociation. The timescale for a wave packet in the ($1e^{-2}$) 3A_2 state to reach the geometry where charge exchange can occur, as well as other details of the dissociation dynamics, precisely explaining the propensity toward fragmentation at H-N-H angles approaching 180° (beyond our qualitative description), would need to be addressed in a future study requiring time-dependent calculations that include nonadiabatic coupling.

In contrast to the three states in Fig. 8 discussed above, the ($1e^{-2}$) 1E state in Fig. 8(c) displays a band of KER over a wide

distribution of θ_{p_1,p_2} extending from 0° to 180° and smoothly peaked toward 180° . This distribution is consistent with the sequential dissociation mechanism discussed below in detail, namely $\text{NH}_3^{2+} \rightarrow \text{NH}^+ + \text{H}^+ + \text{H} \rightarrow \text{N} + 2\text{H}^+ + \text{H}$. If prior to the second step of this process the NH^+ fragment rotates freely before dissociating via a crossing with another electronic state, the H^+ is ejected in a random direction in the body frame of the NH^+ molecule. However, that is not a random direction in the laboratory frame because the NH^+ fragment is translating with a center of mass momentum opposite to the sum of the momenta of the H and H^+ atoms produced in the first step, presumably ejected near the directions of the original NH bonds. The diatom's center of mass is therefore moving away from the H^+ ion produced in the first step, and consequently the random angular distribution of the proton ejected from the moving NH^+ shifted in the direction opposite the direction of the first H^+ ion. A similar effect has been seen in dissociation of the water dication following one-photon double ionization, in which a sequential dissociation channel involving dissociation of OH^+ is seen [38,39].

Other evidence also suggests that the different fragmentation dynamics of the ($1e^{-2}$) 1E state can be specifically attributed to a sequential dissociation mechanism involving four bodies in the final set of fragments. Here, we do not consider the possibility of a sequential dissociation process first resulting in $\text{NH}_2^+ + \text{H}^+$ fragmentation, with the NH_2^+ subsequently dissociating to $\text{NH} + \text{H}^+$ or $\text{N} + \text{H} + \text{H}^+$. Our interpretation does not include these channels, as we have analyzed the $\text{NH}_2^+ + \text{H}^+$ dissociation channel (which is the subject of a future paper) and we did not observe any electron-ion momentum correlation consistent with shared dication electronic states producing both $\text{NH} + \text{H}^+ + \text{H}^+$ or $\text{NH}_2^+ + \text{H}^+$ fragments. However, we cannot totally rule out these possibilities, as the lifetime of the intermediate NH_2^+ fragment may be too short for these fragments to survive the flight time to the ion detector. However, if intermediate NH_2^+ fragments dissociate during their flight to the detector, the secondary-ion momenta should exhibit a broad spread in momentum. Since this is not observed, we argue in favor of a different sequential dissociation mechanism.

Previous measurements have found that PDI to the ($1e^{-2}$) 1E state produces the fragments $\text{NH}^+ + \text{H}^+ + \text{H}$, where the bound NH^+ ion is in its ground state, i.e., the $X^2\Pi$ state [15]. Although the dissociative limit of the $\text{NH}^+ ^2\Pi$ state results in $\text{N}^+(^3P) + \text{H}(^2S)$ fragmentation, it has been shown that the $X^2\Pi$ state crosses the $a^4\Sigma^-$ state in the FC region, and that population transfer between the X and a states can occur via spin-orbit coupling [40–44]. As seen in Fig. 9, the $\text{NH}^+ a^4\Sigma^-$ state dissociates to $\text{H}^+ + \text{N}(^4S)$ with a dissociation energy that is roughly 1 eV smaller than the $X^2\Pi$ state dissociation energy. Thus, high-lying vibrational states of the NH^+ fragment that are initially bound in the $X^2\Pi$ state can undergo intersystem crossing to the $a^4\Sigma^-$ state, yielding the final fragments of the reaction $\text{NH}_3^{2+} \rightarrow \text{N}(^4S) + \text{H}(^2S) + \text{H}^+ + \text{H}^+$. In the present context, population transfer can occur along the inner wall of the quasidegenerate NH^+ states when the initial breakup of the ($1e^{-2}$) 1E state produces $\text{NH}^+(^2\Pi)$ ions with internal energy that lies within the *appearance window* shown in Fig. 9. We can estimate the location of the four-body limit by first extrapolating the

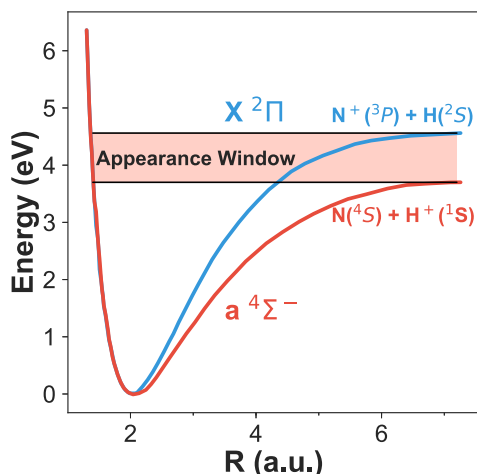


FIG. 9. The potential energy curves for the $X^2\Pi$ ground state and the $a^4\Sigma^-$ state of NH^+ , extracted from Ref. [41]. Population transfer may occur between these states via spin-orbit coupling, where initially bound excitations on the $X^2\Pi$ state can dissociate on the $a^4\Sigma^-$ state. Only diatomic NH^+ fragments with internal energy within (or above) the *appearance window* will dissociate.

MRCI energy for the 3E state (Fig. 1, blue curve) to infinite separation of the N-H bonds. This places the $\text{NH}^+(^4\Sigma^-) + \text{H} + \text{H}^+$ limit at 0.63 eV. Adding to this the 3.66 eV dissociation energy of $\text{NH}^+(^4\Sigma^-)$ places the four-body limit at 4.29 eV, directly in the center of the *appearance window*. This four-body breakup mechanism also explains why the theoretical KER value of 9.42 eV gleaned from Table I is higher than the measured value of 7.7 eV. From Fig. 9 we see that the NH^+ fragment must have a minimum internal energy of 3.7 eV to dissociate to $\text{N} + \text{H}^+$ at the lower end of the appearance window to produce a fast proton with $9.42 - 3.7 \text{ eV} = 5.72 \text{ eV}$ and a zero-energy proton. At the upper end of the *appearance window* we get a fast proton with $9.42 - 4.5 \text{ eV} = 4.92 \text{ eV}$ and a slow proton with 1 eV. This interpretation appears to be consistent with the measured particle energy balance and prompts us to believe that each NH fragment in the three concerted dissociation channels was produced with a distribution of rovibrational energy around 2 eV, while the NH^+ fragment in the sequential dissociation channel was produced with a distribution of rovibrational energy that extends well beyond 3.7 eV, enabling the second fragmentation step. These results are also consistent with a previous theoretical treatment of the dissociation of H_2O^{2+} [45], where the internal energy distribution of the OH^+ fragment in the $\text{H}^+ + \text{OH}^+$ two-body dissociation channel was observed to span approximately 3–5 eV.

Although the initial set of photoions produced via excitation to the $(1e^-)^1E$ state would not produce the four-particle (two-electron, two-proton) coincidence we measure, highly vibrationally excited ground-state NH^+ fragments (lying within the *appearance window*) can spin-orbit couple to a state where a fragmentation, producing a second proton, is possible, yielding the necessary two-proton coincidence. Since the spin-orbit coupling is weak, and the ensuing dissociation is not instantaneous, the intermediate NH^+ fragment can rotate prior to coupling to the dissociative state, which results in a

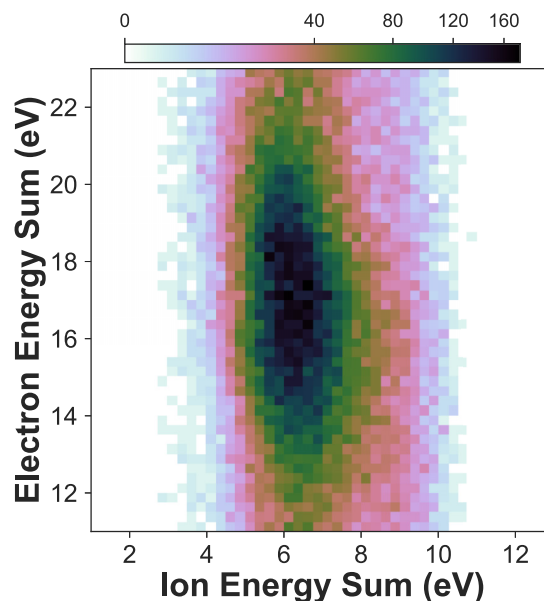


FIG. 10. The yield of $\text{N}^+ + \text{H}^+$ after valence PDI of NH_3 as a function of photoelectron pair energy sum and photoion pair energy sum for the $(1e^-)^1E$ dication state.

proton-proton angular distribution that differs from the other three dication states that involve fewer fragmentation steps. The lifetime of the excited intermediates in the *appearance window* in the $X^2\Pi$ state is determined by the strength of the spin-orbit coupling but is not deduced in our experiment. It could potentially be measured using a different detection scheme or calculated using a different theoretical approach than the one taken in this study.

We discuss the cases of excitations below and above the *appearance window* next. Excitations initially prepared in the $X^2\Pi$ state that lie above the *appearance window* directly dissociate to produce $\text{N}^+(^3P) + \text{H}^+ + \text{H}(^2S) + \text{H}(^2S)$. Indeed, this is supported by our measurements by analyzing the $\text{N}^+ + \text{H}^+$ dissociation channel, which is briefly addressed here. The same procedure used to select the $\text{H}^+ + \text{H}^+$ dissociation channel and described at the beginning of this subsection is used to select the $\text{N}^+ + \text{H}^+$ channel. We plot the PDI yield of the $\text{N}^+ + \text{H}^+$ fragmentation as a function of the photoelectron energy sum and photoion energy sum, shown in Fig. 10. In this fragmentation channel we observe a single feature (seen in Fig. 10), which we attribute to a single contributing dication electronic state. We argue that this feature corresponds to the magenta color-coded $(1e^-)^1E$ state. This feature possesses an electron energy sum of 16.7 eV, which exactly coincides with the electron energy sum measured for the feature in the $\text{H}^+ + \text{H}^+$ dissociation channel corresponding with the $(1e^-)^1E$ state. From this evidence we suggest that the single feature observed in the $\text{N}^+ + \text{H}^+$ channel corresponds with the same dication electronic state that contributes to the sequential $\text{H}^+ + \text{H}^+$ dissociation mechanism. Comparing the $\text{H}^+ + \text{H}^+$ and $\text{N}^+ + \text{H}^+$ yields following PDI to the $(1e^-)^1E$ state indicates that roughly the same amount of population ends up above the *appearance window* as compared to within it. As for excitations initially prepared in the $X^2\Pi$ state that

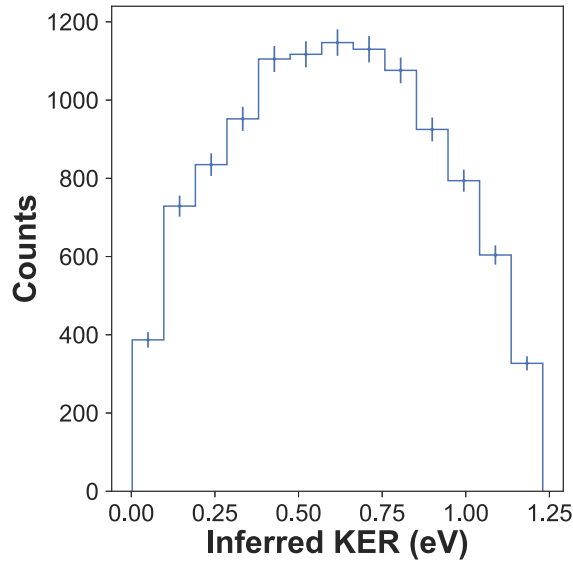


FIG. 11. The inferred KER from the dissociation of the NH^+ fragment, involving the measured slow proton and the nitrogen following PDI of NH_3 at 61.5 eV to the $(1e^-)^1E$ state, resulting in the four-body fragmentation $\text{N} + \text{H} + \text{H}^+ + \text{H}^+$. The KER peaks at 0.61 eV, with a FWHM of 0.71 eV.

lie below the *appearance window*, these will remain as bound NH^+ fragments. This is also supported by our measurements by analyzing the $\text{NH}^+ + \text{H}^+$ dissociation channel (which is the topic of a future paper and thus not presented here). In this dissociation channel we also identify a feature corresponding with the $(1e^-)^1E$ state. These results are entirely consistent with the explanation presented in the paragraph above, where the PDI to the $(1e^-)^1E$ state produces the fragments $\text{NH}^+ \ ^2\Pi + \text{H}^+ + \text{H}$ for which the excitation in the NH^+ ion can lie below, within, or above the *appearance window*. All three of these cases are observed in our measurement and illustrate the various levels of complexity in the dissociation dynamics of simple polyatomic molecules that can occur following valence PDI to just a single state.

To further support the claim that the $\text{H}^+ + \text{H}^+$ fragmentation on the $(1e^-)^1E$ state occurs via the four-body mechanism discussed above, we analyze the slow proton emerging from the dissociation on the $(1e^-)^1E$ state, using its momentum to infer the KER of the dissociation of the NH^+ fragment, shown in Fig. 11. Since two neutral particles are left undetected (N and H), and simple conservation of momentum can thus not be applied, this is realized by assuming that the momentum of the undetected neutral N atom is approximately that of the N-H center of mass, inferred from the two proton momenta. We find the inferred KER to peak at 0.61 eV (FWHM 0.71 eV), which lies below the ~ 1 eV maximum KER permitted by the locations of the two adiabatic limits of the $X^2\Pi$ and $a^4\Sigma^-$ states, i.e., the *appearance window* (see Fig. 9). This supports the assumption that the slow proton emerges from a dissociation on the $a^4\Sigma^-$ state. Since our measurement also indicates that the $(1e^-)^1E$ state contributes to the $\text{NH}^+ + \text{H}^+ + \text{H}$ fragmentation channel (the topic of another manuscript, currently in preparation), which is in agreement with previous measurements [15], we

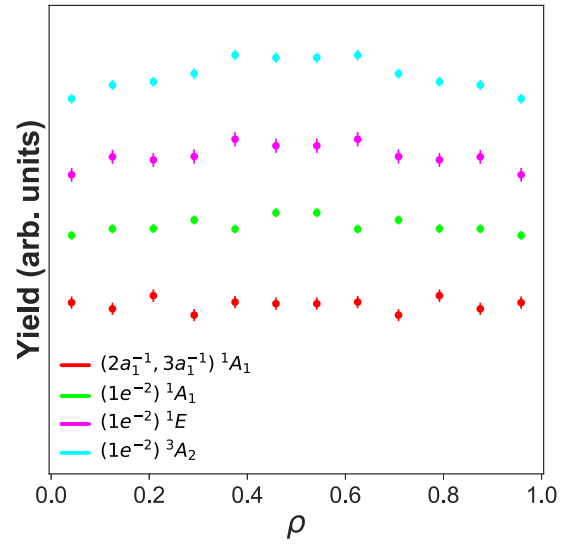


FIG. 12. The yield of the $\text{H}^+ + \text{H}^+$ fragmentation after PDI of NH_3 at 61.5 eV as a function of photoelectron energy sharing for each of the four relevant dication states. Here the y-axis indicates the PDI yield in arbitrary units on a linear scale. The distributions are not internormalized. They have been staggered in order based on their respective electron energy sum for better visibility (i.e., the states are placed in ascending order with respect to their respective photoelectron energy sum).

believe that some small fraction of the NH^+ fragments of this three-body fragmentation channel can decay through intersystem crossing and feed into the four-body $\text{N} + \text{H} + \text{H}^+ + \text{H}^+$ fragmentation channel. This conclusion is also corroborated by our analysis of the $\text{N}^+ + \text{H}^+$ dissociation channel, which shows that the $(1e^-)^1E$ state also feeds into this four-body fragmentation channel and corresponds with the initial excitations in the $\text{NH}^+ \ ^2\Pi$ ion that lie above the *appearance window*.

C. Photoelectron dynamics

Next, we display in Fig. 12 the photoelectron energy-sharing distributions for the four dication states. We define the electron energy sharing as

$$\rho = \frac{E_{e_1}}{E_{e_1} + E_{e_2}}, \quad (1)$$

where E_{e_1} and E_{e_2} are the energies of electrons 1 and 2, respectively. Values of ρ near 0.5 indicate equal energy sharing between the two photoelectrons, while values near 0 or 1 indicate unequal energy sharing between the two photoelectrons. In all four dication states, we do not observe a strong enhancement in yield for any particular values of ρ . The distributions are nearly flat. In the absence of autoionization, this is similar to the PDI of atoms and molecules in this excess energy range (see, e.g., [46,47]). The exception is the $(1e^-)^3A_2$ state (cyan) and perhaps the $(1e^-)^1E$ state (magenta), which show some propensity toward increased yield at values of ρ near 0.5. This is surprising since the $(1e^-)^3A_2$ and the $(1e^-)^1E$ state dication states correspond to the highest electron sum energies (see Fig. 3). A maximum PDI yield at equal energy sharing, if

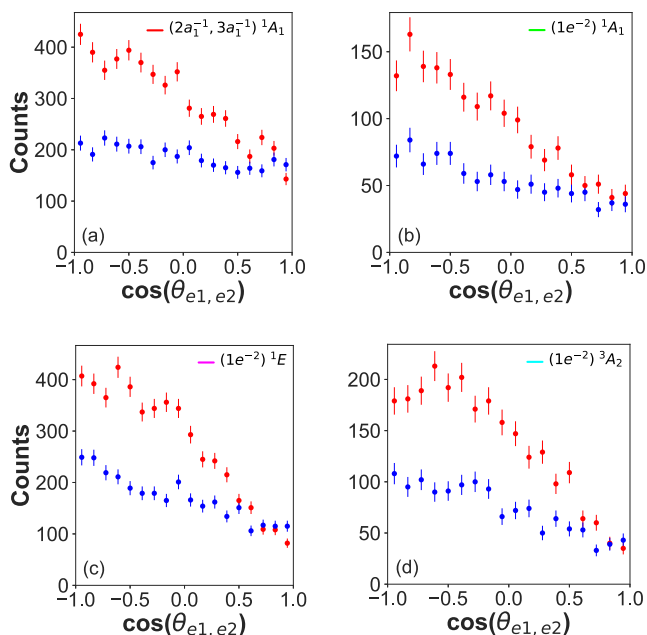


FIG. 13. The cosine of the relative emission angle between the two photoelectrons for two different energy-sharing conditions for each of the four dication states of NH_3 following PDI at 61.5 eV. Electron energy sharing between 0.425 and 0.575 is shown in red, and energy sharing less than 0.05 or greater than 0.95 is shown in blue.

any, would be expected for the lowest electron sum energies according to the Wannier threshold law [48], which favors the emission of two electrons with the same energy and back-to-back close to the PDI threshold. However, the electron pair emission patterns are subject to selection rules that are specific to each dication state and the molecular orientation with respect to the polarization vector; they inherently influence the electron energy sharing to a certain degree. The detailed investigation of this complex problem requires M/RFPADs and is beyond the scope of this work. These distributions have all been normalized to the same value and have been placed in ascending order, based on the corresponding photoelectron energy of the state (the state with the lowest photoelectron energy sum is placed near the bottom and the state with the highest photoelectron energy sum is placed at the top).

Lastly, we plot in Fig. 13 the yield of the $\text{H}^+ + \text{H}^+$ fragmentation as a function of cosine of the relative emission angle between the two photoelectrons and in different energy-sharing conditions of the electron pair for the four dication states, integrated over all molecular orientations relative to the polarization vector of the incoming light and with no restrictions on the emission direction of either electron. The relative electron-electron angles are plotted for $0.425 < \rho < 0.575$ (shown in red) and for $\rho < 0.05$ or $\rho > 0.95$ (shown in blue). We point out that our measurement suffers from some multihit detector deadtime effects, which influence the measured yields of the photoelectrons emitted in the same direction with similar kinetic energies. For equal energy sharing between the two emitted electrons and for $\theta_{e1, e2} \leq 90^\circ$ (emission into the same hemisphere), we can expect to fail to detect up to

$\sim 52\%$ events for the $(1e^-)^2 \ ^3A_2$ state, $\sim 27\%$ for the $(1e^-)^2 \ ^1E$ state, $\sim 23\%$ for the $(1e^-)^2 \ ^1A_1$ state, and $\sim 22\%$ for the $(2a_1^{-1}, 3a_1^{-1}) \ ^1A_1$ state. Note that we estimate these losses for the “worst case” isotropic relative electron-electron emission, which represents very well autoionization processes that are sequential in nature and are subject to unequal energy sharing between the electrons. The equal energy-sharing case, on the other hand, is dominated by knock-out processes with very few electron pairs emitted into the same hemisphere. The actual losses are expected to be closer to the losses for the case of unequal electron energy sharing reported below.

The relative angles between the two photoelectrons under unequal energy-sharing conditions (blue circles in Fig. 13) are rather isotropic for all four dication states, where there is a slight propensity toward back-to-back emission (or in other words a lack of events with electrons emitted into the same direction), which we partly attribute to the deadtime problem at relative electron-electron angles below 90° (emission into the same hemisphere). The simulated losses of events with unequal energy sharing amount to $\sim 26.1\%$ for the $(1e^-)^2 \ ^3A_2$ state, $\sim 8.4\%$ for the $(1e^-)^2 \ ^1E$ state, $\sim 5.2\%$ for the $(1e^-)^2 \ ^1A_1$ state, and $\sim 4.2\%$ for the $(2a_1^{-1}, 3a_1^{-1}) \ ^1A_1$ state. Evidently the small anisotropies in the relative angular distributions for the unequal electron energy-sharing case (blue), presented in Fig. 13 for all four dication states, are accounted for by the detector deadtime limitations, and are otherwise consistent with isotropic relative angular distributions. As there is no hint for autoionization visible in the electron-electron energy correlation map depicted in Fig. 4, the unequal electron energy-sharing case is likely dominated by knock-out processes, as reasoned below.

In contrast, the photoelectron dynamics for equal energy-sharing conditions (red in Fig. 13) reveals anisotropic angular distributions that are different for all four dication states and exceed the anisotropy expected from deadtime effects alone. For this case, the relative angle between the two photoelectrons producing the $(2a_1^{-1}, 3a_1^{-1}) \ ^1A_1$ state exhibits a preference towards back-to-back emission. The emission angle between the two photoelectrons from the $(1e^-)^2 \ ^3A_2$ state increases starting at 0° and peaks at an angle of roughly 125° before decreasing as the angle approaches 180° . The photoelectrons that produce the $(1e^-)^2 \ ^1E$ state have relative emission angles that increase starting at 0° , which then begin to level out at 100° , increasing at a slower rate as the angle approaches 180° . Lastly, the relative electron-electron emission angle of the $(1e^-)^2 \ ^1A_1$ state increases starting at 0° and peaks at an angle of roughly 150° before decreasing as the angle approaches 180° . All four dication states show a non-vanishing PDI yield for small electron-electron angles close to 0° . This contribution is mainly due to the finite angular bin size accepting differences in the relative emission angles of up to 27° at these values, as well as residual background from random coincidences underneath the features visible in, e.g., Fig. 2.

These trends in the relative electron-electron angular distributions as a function of the electron energy sharing possess similarities to prior observations made in the PDI of atomic and molecular targets [6,49–51]. In the valence PDI experiments for helium [49], which is dominated by knock-out processes, rich photoelectron angular distributions emerge

due to selection rules and symmetry considerations. It has been seen that for equal energy-sharing conditions and the first detected electron fixed along the polarization vector of the ionizing field, the relative emission angle between the photoelectrons can be quite anisotropic and peaked at angles between 90° and 180° due to selection rules for dipole-allowed transitions, whereas in unequal energy-sharing conditions the relative angle between the electrons can become more isotropic with a smaller peak at 180° . In the atomic case for equal electron energy sharing, there can be a node at a relative electron-electron angle of 180° , regardless of the emission direction of either of the two electrons. This is true, for instance, for the PDI of He and is due to a selection rule based on parity conservation in one-photon transitions. Such a scenario is in general not well pronounced in the PDI of (polyatomic) molecules, and rather resembles the distributions for all cases presented in Fig. 13. In addition to the finite angular bin size, again accepting differences in the relative emission angles of up to 27° at 180° , we attribute this to the fact that we have not enforced any conditions on the molecular orientation or direction of the polarization vector of the XUV field. Integrating over all molecular orientations and the direction of the polarization vector is prone to washing out sharp features in the electron relative angular distribution, since angular momentum can be transferred to the nuclear systems and softens the aforementioned selection rules (as seen and discussed in Refs. [6,7]), in addition to other features. The limited number of events in the present data set does not allow conditions to be enforced on the molecular orientation or emission direction of one of the photoelectrons with high statistical significance. Future COLTRIMS studies could be directed toward the states that obey the axial recoil approximation to gather appreciable statistics, in order to produce photoelectron angular distributions in the molecular frame, which *inter alia* would help to study and understand the role of selection rules in the PDI of a symmetric top molecule with respect to the polarization vector of the incoming light.

V. CONCLUSION

We have performed state-selective measurements on the $H^+ + H^+$ dissociation channel of NH_3 following direct valence PDI at 61.5 eV, where the two photoelectrons and two protons were measured in coincidence on an event-by-event basis using COLTRIMS. With the assistance of theoretical MRCI calculations of dication PES cuts, we identified the four participating dication electronic states that lead to $H^+ + H^+$ fragmentation, which correspond with the four features we observed, and we have estimated their branching ratios.

The PDI yield as a function of KER and the measured proton-proton angle indicates that three of the four dication states dissociate in a concerted mechanism, while the fourth state, the $(1e^-)^2 \ ^1E$ state, dissociates via a sequential process, with the intermediate ro-vibrationally excited NH^+ fragment ion decaying through an intersystem crossing that leads to a four-body breakup. Two of the dication states, the $(2a_1^{-1}, 3a_1^{-1}) \ ^1A_1$ and $(1e^-)^2 \ ^1A_1$ states, exhibit concerted dissociation mechanisms that fragment near the ground-state geometry (axial recoil approximation applies). The third state, the $(1e^-)^2 \ ^3A_2$ state, undergoes appreciable evolution in its molecular geometry and an asymptotic electron transfer from H to NH^+ at distances greater than 18 Bohr in the dissociating dication, preceding the three-body breakup. Differences between the MRCI calculations and the measured KER suggest that the neutral NH fragment in each of the three-body dissociation channels is highly rovibrationally excited.

The relative emission angle between the two photoelectrons as a function of their energy sharing has some resemblance to prior measurements made on atomic and molecular targets, in spite of integrating over all molecular orientations and emission angles of the first photoelectron, relative to the XUV polarization. While the present study has focused on PDI processes that result in proton-proton breakup channels, we are presently analyzing the two- and three-body PDI breakup channels that produce $NH_2^+ + H^+$ and $NH^+ + H + H^+$, which is the topic of a future manuscript.

ACKNOWLEDGMENTS

This research used resources of the Advanced Light Source (ALS) and the National Energy Research Scientific Computing Center, both being U.S. Department of Energy (DOE) Office of Science (SC) User Facilities under Contract No. DE-AC02-05CH11231. LBNL and JRML personnel were supported by the US DOE SC Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences under contracts DE-AC02-05CH11231 (LBNL) and DE-FG02-86ER13491 (JRML). A.G. was supported by the ALS through a Doctoral Fellowship in Residence. Personnel from the University of Nevada, Reno were supported by the National Science Foundation Grant No. NSF-PHY-1807017. The Frankfurt group acknowledges the support of the Deutsche Akademische Austausch Dienst (DAAD) and the Deutsche Forschungsgemeinschaft (DFG). We thank the staff at the Advanced Light Source for operating the beamline and providing the photon beam. Moreover, we thank the RoentDek GmbH for longtime support with detector hardware and software.

- [1] P. Lablanquie, J. Delwiche, M.-J. Hubin-Franskin, I. Nenner, P. Morin, K. Ito, J. H. D. Eland, J.-M. Robbe, G. Gandara, J. Fournier, and P. G. Fournier, *Phys. Rev. A* **40**, 5673 (1989).
- [2] H. Sann, T. Jahnke, T. Havermeier, K. Kreidi, C. Stuck, M. Meckel, M. S. Schöffler, N. Neumann, R. Wallauer, S. Voss, A. Czasch, O. Jagutzki, T. Weber, H. Schmidt-Böcking, S. Miyabe,

D. J. Haxton, A. E. Orel, T. N. Rescigno, and R. Dörner, *Phys. Rev. Lett.* **106**, 133001 (2011).

- [3] V. Mergel, M. Achler, R. Dörner, K. Khayyat, T. Kambara, Y. Awaya, V. Zoran, B. Nyström, L. Spielberger, J. H. McGuire, J. Feagin, J. Berakdar, Y. Azuma, and H. Schmidt-Böcking, *Phys. Rev. Lett.* **80**, 5301 (1998).

- [4] C. W. McCurdy, D. A. Horner, T. N. Rescigno, and F. Martín, *Phys. Rev. A* **69**, 032707 (2004).
- [5] F. L. Yip, T. N. Rescigno, C. W. McCurdy, and F. Martín, *Phys. Rev. Lett.* **110**, 173001 (2013).
- [6] T. Weber, A. Czasch, O. Jagutzki, A. Müller, V. Mergel, A. Kheifets, J. Feagin, E. Rotenberg, G. Meigs, M. H. Prior, S. Daveau, A. L. Landers, C. L. Cocke, T. Osipov, H. Schmidt-Böcking, and R. Dörner, *Phys. Rev. Lett.* **92**, 163001 (2004).
- [7] W. Vanroose, D. A. Horner, F. Martín, T. N. Rescigno, and C. W. McCurdy, *Phys. Rev. A* **74**, 052702 (2006).
- [8] B. Gaire, S. Y. Lee, D. J. Haxton, P. M. Pelz, I. Bocharova, F. P. Sturm, N. Gehrken, M. Honig, M. Pitzer, D. Metz, H.-K. Kim, M. Schöffler, R. Dörner, H. Gassert, S. Zeller, J. Voigtsberger, W. Cao, M. Zohrabi, J. Williams, A. Gatton, D. Reedy, C. Nook, T. Müller, A. L. Landers, C. L. Cocke, I. Ben-Itzhak, T. Jahnke, A. Belkacem, and T. Weber, *Phys. Rev. A* **89**, 013403 (2014).
- [9] J. Rajput, T. Severt, B. Berry, B. Jochim, P. Feizollah, B. Kaderiya, M. Zohrabi, U. Ablikim, F. Ziaee, K. Raju P., D. Rolles, A. Rudenko, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Phys. Rev. Lett.* **120**, 103001 (2018).
- [10] R. N. Zare, *Mol. Photochem.* **4**, 1 (1972).
- [11] T. Weber, A. O. Czasch, O. Jagutzki, A. Müller, V. Mergel, A. Kheifets, E. Rotenberg, G. Meigs, M. H. Prior, S. Daveau *et al.*, *Nature (London)* **431**, 437 (2004).
- [12] D. Akoury, K. Kreidi, T. Jahnke, T. Weber, A. Staudte, M. Schöffler, N. Neumann, J. Titze, L. P. H. Schmidt, A. Czasch *et al.*, *Science* **318**, 949 (2007).
- [13] T. J. Reddish, J. Colgan, P. Bolognesi, L. Avaldi, M. Gisselbrecht, M. Lavollée, M. S. Pindzola, and A. Huetz, *Phys. Rev. Lett.* **100**, 193001 (2008).
- [14] D. Winkoun and G. Dujardin, *Z. Phys. D* **4**, 57 (1986).
- [15] M. Stankiewicz, P. A. Hatherly, L. J. Frasinski, K. Codling, and D. M. P. Holland, *J. Phys. B* **22**, 21 (1989).
- [16] R. Locht, M. Davister, W. Denzer, H. Jochims, and H. Baumgärtel, *Chem. Phys.* **138**, 433 (1989).
- [17] R. Locht and J. Momigny, *Chem. Phys. Lett.* **138**, 391 (1987).
- [18] J. H. Eland, *Chem. Phys.* **323**, 391 (2006).
- [19] J. A. Samson, G. Haddad, and L. Kilcoyne, *J. Chem. Phys.* **87**, 6416 (1987).
- [20] J. Appell and J. Horsley, *J. Chem. Phys.* **60**, 3445 (1974).
- [21] T. Märk, F. Egger, and M. Cheret, *J. Chem. Phys.* **67**, 3795 (1977).
- [22] M. Langford, F. Harris, P. Fournier, and J. Fournier, *Int. J. Mass Spectrom. Ion Proc.* **116**, 53 (1992).
- [23] W. Griffiths and F. Harris, *Rapid Commun. Mass Spectrom.* **4**, 366 (1990).
- [24] R. Locht, C. Servais, M. Ligot, F. Derwa, and J. Momigny, *Chem. Phys.* **123**, 443 (1988).
- [25] J. White, R. Rye, and J. Houston, *Chem. Phys. Lett.* **46**, 146 (1977).
- [26] R. Camilloni, G. Stefani, and A. Giardini-Guidoni, *Chem. Phys. Lett.* **50**, 213 (1977).
- [27] M. T. Økland, K. Fægri Jr., and R. Manne, *Chem. Phys. Lett.* **40**, 185 (1976).
- [28] D. R. Jennison, *Phys. Rev. A* **23**, 1215 (1981).
- [29] R. Boyd, S. Singh, and J. Beynon, *Chem. Phys.* **100**, 297 (1985).
- [30] R. Dörner, V. Mergel, O. Jagutzki, L. Spielberger, J. Ullrich, R. Moshhammer, and H. Schmidt-Böcking, *Phys. Rep.* **330**, 95 (2000).
- [31] J. Ullrich, R. Moshhammer, A. Dorn, R. Dörner, L. P. H. Schmidt, and H. Schmidt-Böcking, *Rep. Prog. Phys.* **66**, 1463 (2003).
- [32] O. Jagutzki, A. Cerezo, A. Czasch, R. Dörner, M. Hattas, M. Huang, V. Mergel, U. Spillmann, K. Ullmann-Pflegler, T. Weber *et al.*, *IEEE Trans. Nucl. Sci.* **49**, 2477 (2002).
- [33] S. A. Pope, I. H. Hillier, M. F. Guest, and J. Kendrick, *Chem. Phys. Lett.* **95**, 247 (1983).
- [34] F. Tarantelli, A. Tarantelli, A. Sgamellotti, J. Schirmer, and L. S. Cederbaum, *Chem. Phys. Lett.* **117**, 577 (1985).
- [35] T. N. Rescigno, C. S. Trevisan, A. E. Orel, D. S. Slaughter, H. Adaniya, A. Belkacem, M. Weyland, A. Dorn, and C. W. McCurdy, *Phys. Rev. A* **93**, 052704 (2016).
- [36] T. N. Rescigno and B. I. Schneider, *J. Phys. B* **21**, L691 (1988).
- [37] J. Higuchi, *J. Chem. Phys.* **24**, 535 (1956).
- [38] Z. L. Streeter, F. L. Yip, R. R. Lucchese, B. Gervais, T. N. Rescigno, and C. W. McCurdy, *Phys. Rev. A* **98**, 053429 (2018).
- [39] I. Ben-Itzhak and T. Severt (private communication, 2020).
- [40] H. Liu and G. Verhaegen, *J. Chem. Phys.* **53**, 735 (1970).
- [41] J. M. Amero and G. J. Vázquez, *Int. J. Quantum Chem.* **99**, 353 (2004); **101**, 396 (2005).
- [42] K. Kawaguchi and T. Amano, *J. Chem. Phys.* **88**, 4584 (1988).
- [43] R. Colin and A. Douglas, *Can. J. Phys.* **46**, 61 (1968).
- [44] R. Tarroni, P. Palmieri, A. Mitrushenkov, P. Tosi, and D. Bassi, *J. Chem. Phys.* **106**, 10265 (1997).
- [45] B. Gervais, E. Giglio, L. Adoui, A. Cassimi, D. Duflot, and M. Galassi, *J. Chem. Phys.* **131**, 024302 (2009).
- [46] J. Andersson, S. Zagorodskikh, A. H. Roos, O. Talae, R. Squibb, D. Koulentianos, M. Wallner, V. Zhaunerchyk, R. Singh, J. Eland *et al.*, *Sci. Rep.* **9**, 1 (2019).
- [47] D. Reedy, J. B. Williams, B. Gaire, A. Gatton, M. Weller, A. Menssen, T. Bauer, K. Henrichs, P. Burzynski, B. Berry, Z. L. Streeter, J. Sartor, I. Ben-Itzhak, T. Jahnke, R. Dörner, T. Weber, and A. L. Landers, *Phys. Rev. A* **98**, 053430 (2018).
- [48] G. H. Wannier, *Phys. Rev.* **90**, 817 (1953).
- [49] H. Bräuning, R. Dörner, C. L. Cocke, M. H. Prior, B. Krässig, A. S. Kheifets, I. Bray, A. Bräuning-Demian, K. Carnes, S. Dreuil, V. Mergel, P. Richard, J. Ullrich, and H. Schmidt-Böcking, *J. Phys. B* **31**, 5149 (1998).
- [50] A. Knapp, B. Krässig, A. Kheifets, I. Bray, T. Weber, A. L. Landers, S. Schössler, T. Jahnke, J. Nickles, S. Kammer, O. Jagutzki, L. P. H. Schmidt, M. Schöffler, T. Osipov, M. H. Prior, H. Schmidt-Böcking, C. L. Cocke, and R. Dörner, *J. Phys. B* **38**, 645 (2005).
- [51] J. M. Randazzo, G. Turri, P. Bolognesi, J. Mathis, L. U. Ancarani, and L. Avaldi, *Phys. Rev. A* **101**, 033407 (2020).

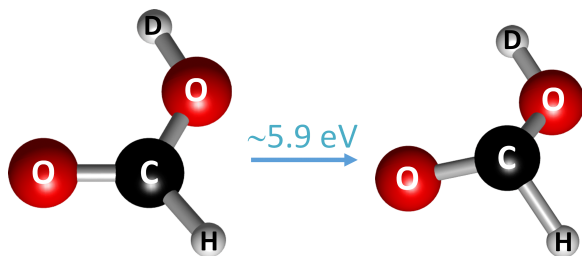


Figure 3.4: (Left) The initial configuration of planar formic acid HCOOD . (Right) The pyramidalization of HCOOD after absorbing 5.9 eV. Specifically, the C atom moves out of the initial molecular plane.

3.6 Towards four-body sequential fragmentation

In this section, we present the 4-body fragmentation of formic acid following its quadruple ionization by an intense laser field. Specifically, we study the HCOOD isotopologue shown in Fig. 3.4, which fragments into $\text{H}^+ + \text{D}^+ + \text{O}^+ + \text{CO}^+$. The advantage of this molecule is that it is relatively simple, only containing 5 constituent atoms, and is initially planar. The hope is that the initial planar configuration confines any resulting sequential fragmentation dynamics to a plane, enabling their identification using the approaches previously discussed in this chapter.

3.6.1 Four-body Jacobi coordinates and their conjugate momenta

Below we provide the framework for generalizing the Jacobi coordinates and their conjugate momenta to four-body breakup. In Fig. 3.5, we show the two possible classes of four-body Jacobi coordinates [134]. Specifically, in Fig. 3.5(a), we show the H-type coordinates for an arbitrary ABCD molecule⁵, where $\boldsymbol{\rho}_{\text{AB}}$ and $\boldsymbol{\rho}_{\text{CD}}$ represent the relative coordinates between the A and B as well as the C and D fragments, respectively. In this case, $\boldsymbol{\rho}_{\text{AB,CD}}$ is the coordinate between the center-of-mass of the AB and CD fragments and $\mathbf{X}$ is the coordinate of the center-of-mass of the whole molecule. It is important to note that since we analyze our imaging data in the center-of-mass frame of the recoiling molecular ion (see Section 2.3.1), we do not need to keep track of $\mathbf{X}$ and its corresponding momentum. Therefore, we omit

⁵Note that the A, B, C, and D fragments can either be atomic or molecular fragments. In the case that the label represents a molecular fragment, the coordinate goes to the center-of-mass of the fragment.

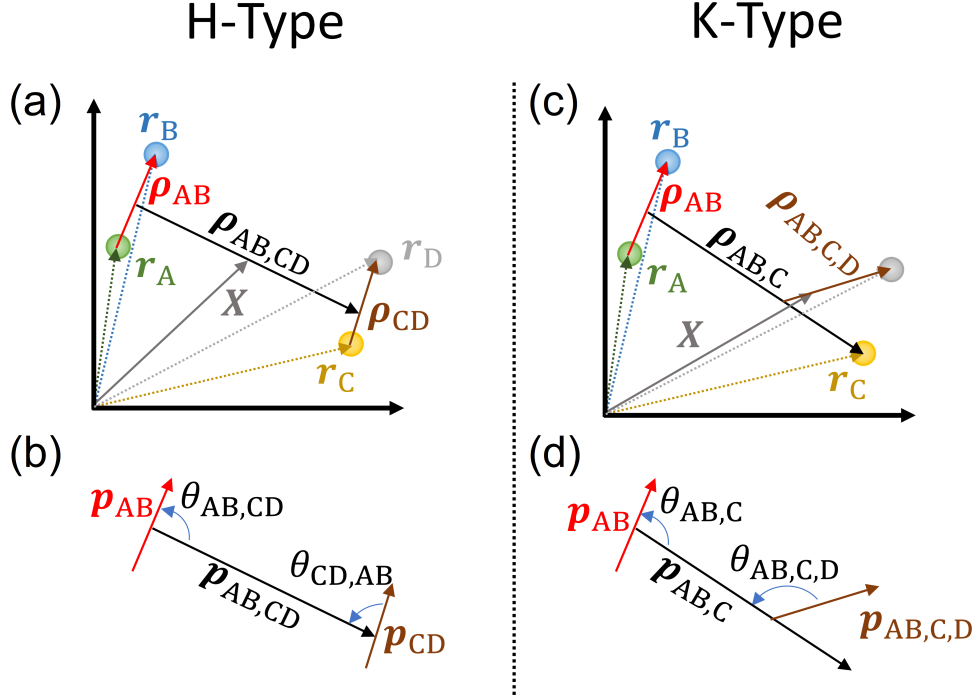


Figure 3.5: Panels (a) and (b) display the H-type Jacobi coordinates and their conjugate momenta, respectively, for an arbitrary ABCD molecule. Similarly, panels (c) and (d) display the K-type Jacobi coordinates and their conjugate momenta, respectively.

this coordinate from any further discussion. The equations describing the Jacobi coordinates are

$$\boldsymbol{\rho}_{AB} = \mathbf{r}_B - \mathbf{r}_A, \quad (3.6)$$

$$\boldsymbol{\rho}_{CD} = \mathbf{r}_D - \mathbf{r}_C, \quad (3.7)$$

$$\boldsymbol{\rho}_{AB,CD} = \frac{1}{m_{CD}} (m_C \mathbf{r}_C + m_D \mathbf{r}_D) - \frac{1}{m_{AB}} (m_A \mathbf{r}_A + m_B \mathbf{r}_B), \quad (3.8)$$

where m_{AB} and m_{CD} are the total mass of the AB and CD intermediate fragments, respectively.

The resulting conjugate momenta, shown schematically in Fig. 3.5(b), are given by:

$$\mathbf{p}_{AB} = \mu_{AB} \dot{\boldsymbol{\rho}}_{AB} = \mu_{AB} (\mathbf{P}_B/m_B - \mathbf{P}_A/m_A), \quad (3.9)$$

$$\mathbf{p}_{CD} = \mu_{CD} \dot{\boldsymbol{\rho}}_{CD} = \mu_{CD} (\mathbf{P}_D/m_D - \mathbf{P}_C/m_C), \quad (3.10)$$

$$\mathbf{p}_{AB,CD} = \mu_{AB,CD} \dot{\boldsymbol{\rho}}_{AB,CD} = \mathbf{P}_C + \mathbf{P}_D, \quad (3.11)$$

where μ_{AB} and μ_{CD} represent the reduced masses of the AB and CD molecules, respectively, while $\mu_{AB,CD}$ also represents a reduced mass given explicitly by

$$\mu_{AB,CD} = \left(\frac{1}{m_{AB}} + \frac{1}{m_{CD}} \right)^{-1}. \quad (3.12)$$

We believe this choice would be most natural when two possible intermediates (AB and CD) are formed together or where only one of these intermediates is formed.

Alternatively, one can choose to use the K-type Jacobi coordinates, shown in Fig. 3.5(c). The coordinates are explicitly defined as

$$\boldsymbol{\rho}_{AB} = \mathbf{r}_B - \mathbf{r}_A, \quad (3.13)$$

$$\boldsymbol{\rho}_{AB,C} = \mathbf{r}_C - \frac{1}{m_{AB}} (m_A \mathbf{r}_A + m_B \mathbf{r}_B), \quad (3.14)$$

$$\boldsymbol{\rho}_{ABC,D} = \mathbf{r}_D - \frac{1}{m_{ABC}} (m_A \mathbf{r}_A + m_B \mathbf{r}_B + m_C \mathbf{r}_C), \quad (3.15)$$

where m_{ABC} is the total mass of the ABC molecule. The resulting conjugate momenta, shown schematically in Fig. 3.5(d), are given by:

$$\mathbf{p}_{AB} = \mu_{AB} \dot{\boldsymbol{\rho}}_{AB} = \mu_{AB} (\mathbf{P}_B/m_B - \mathbf{P}_A/m_A), \quad (3.16)$$

$$\mathbf{p}_{AB,C} = \mu_{AB,C} \dot{\boldsymbol{\rho}}_{AB,C} = \mathbf{P}_C + \frac{m_C}{m_{ABC}} \mathbf{P}_D, \quad (3.17)$$

$$\mathbf{p}_{ABC,D} = \mu_{ABC,D} \dot{\boldsymbol{\rho}}_{ABC,D} = \mathbf{P}_D. \quad (3.18)$$

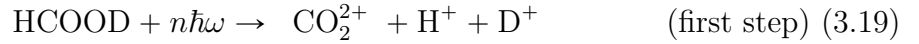
This choice of coordinates may be most useful for analyzing sequential fragmentation with consecutive fragmentation steps, i.e. when the ABCD molecule first breaks into ABC + D, followed by ABC breaking to AB + C, and finally the AB breaks into A + B. This is also useful for sequential fragmentation with only one step like ABCD first breaking into ABC + D, followed by ABC breaking directly into A + B + C.

Since we are dealing with 4-body breakup, the conjugate momenta are not guaranteed to lie in a plane, contrary to the three-body case, possibly leading to further complications with using rotation in the fragmentation plane as a signature. In this section, we show some

preliminary data suggesting that rotation outside the fragmentation plane may be affecting our signature of sequential breakup.

3.6.2 Four-body fragmentation of HCOOD

Below, we consider the strong-field⁶ induced four-body fragmentation of HCOOD^{4+} into $\text{H}^+ + \text{D}^+ + \text{O}^+ + \text{CO}^+$. Since we only measure four fragments, we use the four-body conjugate momenta described in the previous subsection, where the momenta of CO^+ fragment goes to its center-of-mass. In this fragmentation channel, the most likely intermediate is a CO_2^{2+} molecule, which is known to be metastable [135–139]. Specifically, we are investigating the sequential fragmentation channel occurring via



As further evidence supporting this breakup process, we also observe the $\text{H}^+ + \text{D}^+ + \text{CO}_2^{2+}$ breakup channel, indicating that some of the CO_2^{2+} molecules are populated in states with lifetimes long enough to survive their flight to the detector, similar to what we saw with CO^{2+} and CS^{2+} from OCS (see Section 3.4). For brevity, we only consider the CO_2^{2+} intermediate below. It is important to note that we did look for signatures of other possible intermediates, but did not observe any convincing evidence for them.

In Fig. 3.6(a), we show the $N(\text{KER}_{\text{CO}_2}, \theta_{\text{CO}_2, \text{HD}})$ distribution, using the H-type conjugate momenta, assuming a CO_2^{2+} intermediate is formed. Note that KER_{CO_2} is defined as

$$\text{KER}_{\text{CO}_2} = \frac{\mathbf{p}_{\text{CO}_2}^2}{2\mu_{\text{CO}_2}} \quad (3.21)$$

where

$$\mu_{\text{CO}_2} = \left(\frac{1}{m_{\text{CO}}} + \frac{1}{m_{\text{O}}} \right)^{-1} \quad (3.22)$$

⁶The peak intensity of the 780-nm laser field is around 10^{15} W/cm².

and

$$\mathbf{p}_{\text{CO}_2} = \mu_{\text{CO}_2} (\mathbf{P}_{\text{CO}}/m_{\text{CO}} - \mathbf{P}_{\text{O}}/m_{\text{O}}) \quad (3.23)$$

First, we observe a concerted fragmentation structure located at small angles. On the other hand, there appears to be a broad angular distribution spanning from 60° to 180° , perhaps hinting that sequential fragmentation occurs. In Fig. 3.6(b), we show the $N(\theta_{\text{CO}_2,\text{HD}})$ distribution integrated over all KER_{CO_2} in black. However, the resulting angular distribution is not as flat as the typical signature of sequential fragmentation discussed previously in this chapter. Instead, it follows a similar behavior to the simulations included in Appendix A of the paper included in Section 3.4. To understand why, we need to look more carefully at the structure of formic acid.

As shown in Fig. 3.4, the equilibrium geometry of neutral formic acid is planar. However, it is known that at about 5.9 eV, there lies a state in which the C atom is lifted out of the plane [140–142], i.e. the pyramidalization of the molecule, making the molecule chiral [143]. Given that our photon energies are around 1.5 eV, this corresponds to near resonant four-photon absorption, suggesting that this transition can occur early in the pulse. Furthermore, researchers have shown that this photoinduced chirality can be observed using similarly intense laser fields [143]. Therefore, since the formic acid molecule likely becomes nonplanar during its interaction with the laser, we should not expect a uniform angular distribution in Figs. 3.6(a) and (b). In the future, it will be beneficial to ionize the molecule with wavelengths that circumvent this state, such as with a 266-nm field.

Given that it is not clear which Jacobi coordinate type (H or K) would better identify sequential breakup in this case, we also show the $N(\text{KER}_{\text{CO}_2}, \theta_{\text{CO}_2,\text{D}})$ and $N(\theta_{\text{CO}_2,\text{D}})$ distributions using the K-type relative momenta in Figs. 3.6(c) and (d), respectively. Here, the distribution looks much different, which likely comes from the polar angle $\theta_{\text{CO}_2,\text{D}}$ being plotted using a different coordinate system than $\theta_{\text{CO}_2,\text{HD}}$. However, further work is required to fully comprehend why certain coordinate system choices are better than others.

Overall, our four-body breakup results of HCOOD^{4+} breaking into $\text{H}^+ + \text{D}^+ + \text{O}^+ + \text{CO}^+$ look encouraging. However, more work needs to be done to confirm that sequential fragmen-

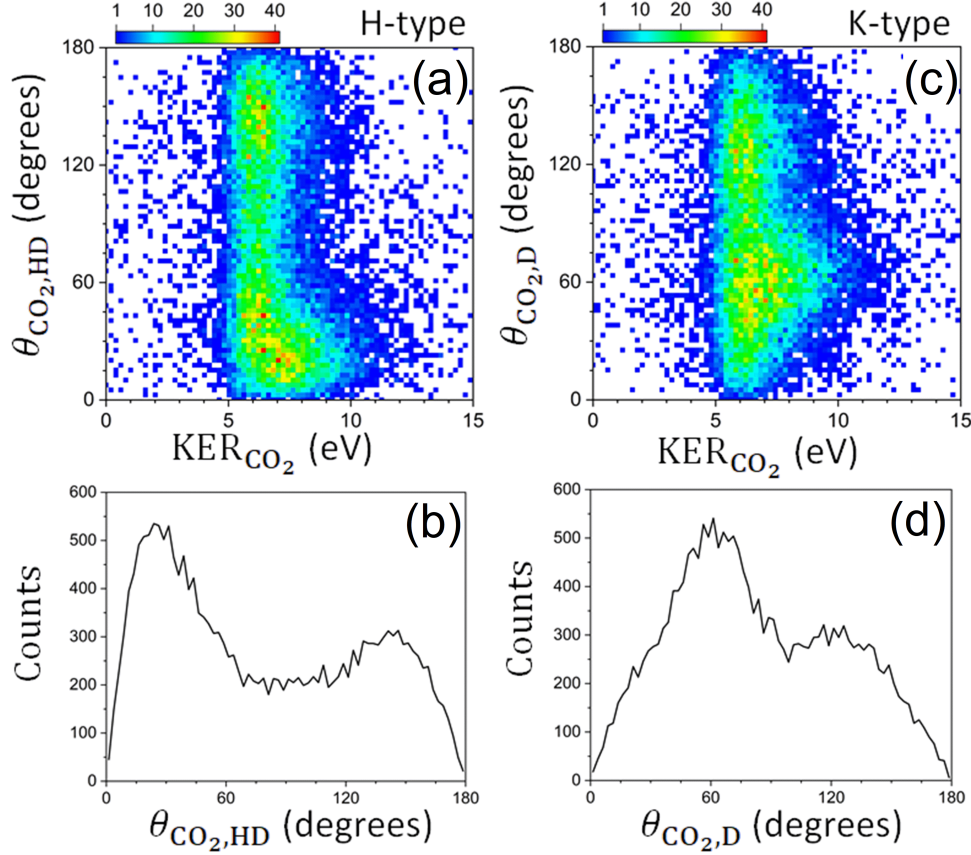


Figure 3.6: Plots displaying events of HCOOD^{4+} breaking into $\text{H}^+ + \text{D}^+ + \text{C}^+ + \text{CO}^+$, where we are looking for sequential fragmentation via a CO_2^{2+} intermediate. Panels (a) and (b) display the $N(\text{KER}_{\text{CO}_2}, \theta_{\text{CO}_2, \text{HD}})$ and $N(\theta_{\text{CO}_2, \text{HD}})$ distributions calculated using the H-type Jacobi coordinates. Panels (c) and (d) plot the $N(\text{KER}_{\text{CO}_2}, \theta_{\text{CO}_2, \text{D}})$ and $N(\theta_{\text{CO}_2, \text{D}})$ distributions calculated using the K-type Jacobi coordinates.

tation occurs via a CO_2^{2+} intermediate. Some open questions are why the H type coordinates appear to be a better coordinate choice than the K type coordinates in this case as well as what is the best signature for identifying sequential breakup.

3.7 Summary and outlook

In this chapter, we presented our newly developed native frames method for analyzing multi-body fragmentation and extended it to identify signatures of sequential breakup. In most of our work, we showed the strength of the method using three-body fragmentation as an example. Specifically, the signature of sequential fragmentation is a uniform distribution

of the angle between the conjugate momenta describing each fragmentation step. We then exploited this uniform angular distribution to reconstruct parts of the sequential distribution masked by other competing processes on an event-by-event basis. With this information, one can separate the sequential and concerted distributions in any plot created from the measured momenta as well as determine the branching ratios of concerted and sequential breakup.

In addition, we took advantage of how the native frames method naturally analyzes sequential fragmentation in each fragmentation step to explore the step-by-step dynamics. Using a single-photon induced double-ionization of D_2O as an example, we followed the dynamics step-by-step and state-selectively. Furthermore, using the theoretical results, we deduced the rotational population of the intermediate fragments and show that this population is imprinted in the threshold behavior of the second fragmentation step's KER.

In addition, we expanded our analysis to the nonplanar ammonia molecule, where we used a different signature to identify sequential fragmentation. Finally, we provided the framework for extending the native-frames analysis to 4-body breakup and showed some promising preliminary results for the sequential breakup formic acid (HCOOD).

Chapter 4

Bond rearrangement in polyatomic molecules

In this chapter, we discuss our studies focusing on the bond rearrangement in polyatomic molecules induced by a strong laser field. Specifically, we explore bond-rearrangement due to the isomerization in several triatomic molecules. In addition, we study the formation of H_3^+ from various alcohols, specifically investigating the role of H_2 roaming.

4.1 Introduction

Bond rearrangement in polyatomic molecules can occur via isomerization, i.e. a process where the molecule's configuration changes while retaining its constituent atoms [144]. The various configurations, which are known as isomers, typically have different chemical properties [145] and find use throughout nature [111, 112, 146] and industry [108, 110]. One exciting example is a molecular switch [147], which can isomerize between two or more states reversibly and can be initiated via many environmental stimuli, such as pH, light, electrical current, temperature, and more. Furthermore, isomerization followed by the dissociation of a molecule has been suggested as a way to create useful compounds from the atomic constituents of the molecule, such as converting CO_2 into O_2 [148]. Below, we study isomer-

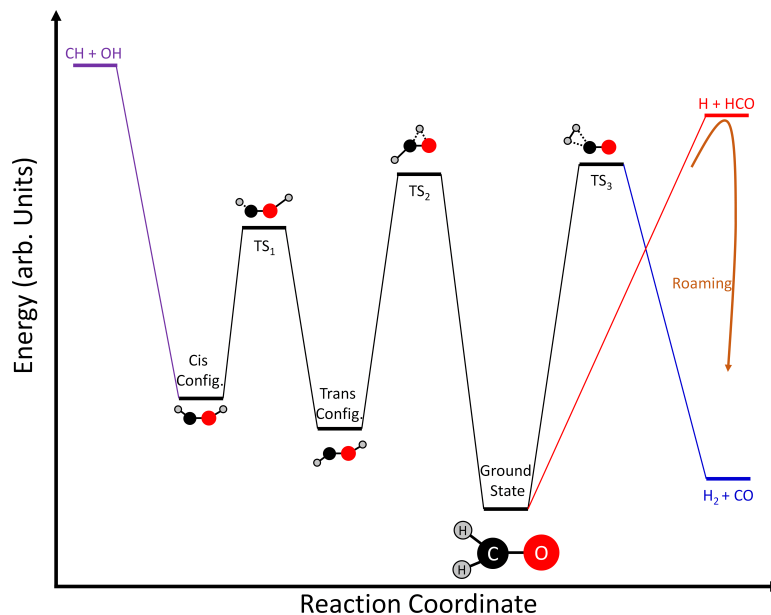


Figure 4.1: A schematic transition-state picture for the isomerization and dissociation of the formaldehyde (H_2CO) molecule. Furthermore, a competing roaming pathway to the $\text{H}_2 + \text{CO}$ dissociation limit that circumvents the TS_3 transition state by first going to the $\text{H} + \text{HCO}$ dissociation limit (figure is adapted from Ref. [152] with the addition of the $\text{CH} + \text{OH}$ dissociation limit to introduce isomerization).

ization processes in “simple” molecules, where the signatures of isomerization are observed in the molecules’ fragmentation channels.

It has been shown that the bond rearrangement of molecules can occur via two competing mechanisms, through transition states [149, 150] or roaming [151, 152]. To help explain these two mechanisms, we focus on the prototypical example of formaldehyde (H_2CO), where both mechanisms compete leading to the $\text{H}_2 + \text{CO}$ fragmentation channel [151–153].

A common way to understand molecular dynamics is through transition-state theory [149, 150], where an intrinsic concept is the reaction coordinate, i.e. the minimum energy path connecting the reactants to the products [149–151]. Along the reaction coordinate, one encounters various saddle points, i.e. local maxima in the potential energy along the reaction coordinate known as transition states, that need to be overcome. The strength of transition state theory is that it allows one to connect the quantum behavior of the molecule to the macroscopic rates of the chemical reactions [151]. As a result, this theory has been widely adopted throughout the chemistry community [149–152, 154, 155].

In Fig. 4.1, we show the transition states of the neutral formaldehyde molecule [152]. Specifically, the figure shows an example reaction pathway leading to the isomerization and fragmentation of formaldehyde into $\text{CH} + \text{OH}$ on the left side of the figure. Beginning in the ground state H_2CO geometry, one of the hydrogens migrates from the carbon atom to the oxygen atom, eventually forming HCOH in a trans configuration. The dynamics then continue, overcoming transition state TS_1 and forming HCOH in its cis configuration. Finally, the molecule fragments into $\text{CH} + \text{OH}$.

On the other hand, roaming may also occur. However, to explain roaming, we first need to discuss the reaction pathways leading to the $\text{H} + \text{HCO}$ and $\text{H}_2 + \text{CO}$ fragmentation channels. Specifically, from the ground state H_2CO configuration, one reaction pathway links directly to the $\text{H} + \text{HCO}$ limit. On the other hand, to form $\text{H}_2 + \text{CO}$, the molecule must fragment along a different reaction coordinate and overcome a transition state (labeled TS_3 in Fig. 4.1) before reaching the dissociation limit.

Roaming can also contribute to the $\text{H}_2 + \text{CO}$ dissociation limit [151–153]. Specifically, roaming describes a pathway which does not follow the minimum energy route and can circumvent transition states, such as TS_3 in Fig. 4.1. In the case of formaldehyde, roaming begins along the reaction coordinate going to the $\text{H} + \text{HCO}$ dissociation limit. However, instead of dissociating, the H fragment remains weakly bound and “orbits” around the remaining molecule until it eventually (usually after a few 100 femtoseconds) abstracts the remaining H and dissociates as an $\text{H}_2 + \text{CO}$. Because the abstraction occurs at large $\text{H}-\text{H}$ distances, the resulting H_2 molecule is vibrationally excited, which is the signature distinguishing the roaming pathway from the direct reaction pathway to the $\text{H}_2 + \text{CO}$ dissociation limit [153]. The roaming pathway is shown schematically in Fig. 4.1 by the burnt orange arrow.

The important consequence of roaming is that it is not accounted for in the transition state theory [151, 152]. Since this theory is predominantly used to determine macroscopic reaction rates, the omission of roaming can lead to significantly incorrect results, especially when roaming plays a dominant role [156]. Therefore, there have been extensive studies of the dynamics of roaming and how to incorporate it theoretically [151–153, 156–159].

We use the COLTRIMS technique (see Section 2.3) to study the bond rearrangement and fragmentation of various molecules in this chapter. It is important to note that in our experiments, we cannot distinguish roaming from bond-rearrangement due to isomerization because we cannot experimentally determine the internal energy of the resulting fragments. However, in some cases, we have theoretical support showing that roaming is at least a contributing mechanism. Specifically, we study the bond rearrangement of triatomic molecules (see Section 4.2) and the formation of H_3^+ due to H_2 roaming in several alcohol molecules (Section 4.3).

4.2 Bond rearrangement in triatomic molecules

Here, we present our publication in *Physical Review A* about bond rearrangement of the OCS, CO_2 and H_2O molecules induced by strong laser fields under similar laser conditions. For example, in the case of OCS^{2+} , we study the $\text{SO}^+ + \text{C}^+$ fragmentation channel, which can occur via OCS^{2+} isomerizing into CSO^{2+} [160]. To compare the bond-rearrangement channels between different molecules, we calculate the branching ratios taking into account all non-negligible one-, two-, and three-body breakup channels resulting from the double-ionization of the parent molecule. Furthermore, by using branching ratios, we account for changes in the target density as well as the difference in the strong-field double-ionization probability, at least in first order. We find that the bond-rearrangement channels have approximately the same branching ratio (on the order of 0.1%), perhaps suggesting similar formation mechanisms.

The data we used in this paper were collected by various other group members in their studies of different fragmentation dynamics. For example, the OCS and CO_2 data sets were acquired by Jyoti Rajput and Peyman Feizollah, respectively, to study three-body sequential fragmentation following triple-ionization. While assisting with the others' analysis, I discovered the bond-rearrangement channels and suggested that analyzing these channels would be a good project for our summer undergraduate student Shitong Zhao. I mentored him throughout the summer, teaching him to analyze the data and assisted him and Eric Wells

in writing the paper.

Strong-field-induced bond rearrangement in triatomic molecules

S. Zhao,¹ Bethany Jochim,² Peyman Feizollah,² Jyoti Rajput,^{2,*} F. Ziaee,² Kanaka Raju P.,² B. Kaderiya,² K. Borne,² Y. Malakar,² Ben Berry,² J. Harrington,² D. Rolles,² A. Rudenko,² K. D. Carnes,² E. Wells,^{1,†} I. Ben-Itzhak,^{2,‡} and T. Severt^{2,§}

¹*Department of Physics, Augustana University, Sioux Falls, South Dakota 57197, USA*

²*J. R. Macdonald Laboratory, Physics Department, Kansas State University, Manhattan, Kansas 66506, USA*



(Received 14 February 2019; published 15 May 2019)

A comparative study of bond rearrangement is reported for the double ionization of three triatomic molecules: carbon dioxide, carbonyl sulfide, and water (D_2O). Specifically, we study the formation of the molecular cation AC^+ from the edge atoms of a triatomic molecular dication ABC^{2+} following double ionization by intense, short (23 fs, 790 nm) laser pulses. The comparison is made using the double ionization branching ratio of each molecule, thereby minimizing differences due to differing ionization rates. The rearrangement branching ratio is highest for water, which has a bent initial geometry, while CO_2 and OCS are linear molecules. The angular distribution of O_2^+ fragments arising from CO_2 is essentially isotropic, while SO^+ from OCS and D_2^+ from D_2O are aligned with the laser polarization. In the CO_2 and D_2O cases, the angular distributions of the bond rearrangement channels are different from the angular distributions of the dominant dissociative double ionization channels $CO^+ + O^+$ and $OD^+ + D^+$. Only the angular distribution of SO^+ from OCS is both aligned with the laser polarization and similar to the angular distribution of the largest dissociative channel, $CO^+ + S^+$. The mixed behavior observed from the angular distributions of the different molecules stands in contrast to the relative consistency of the magnitude of the bond rearrangement branching ratio.

DOI: [10.1103/PhysRevA.99.053412](https://doi.org/10.1103/PhysRevA.99.053412)

I. INTRODUCTION

The breaking and subsequent formation of new molecular bonds in unimolecular chemical reactions has attracted considerable attention in recent years [1–30]. Examples of such processes include roaming [4,10,13,17,19,24], in which a neutral moiety traverses the molecule to capture another atom, hydrogen migration [9,12,15,16,18,20,21,25], and bond rearrangement [1,3,5–8,11,14,22,23,28,30], in which the cleaving of multiple bonds initiates a process leading to the formation of a new molecule from atoms that were not previously bonded to each other. A number of prominent photochemical reactions involve these processes, including decomposition of water [31] or NO_3 [32,33] by photolysis, the conversion of carbon dioxide to oxygen in the atmosphere [26,34], the combustion of hydrocarbons [12,15,20,25], and the formation of H_3^+ from alcohols [10,24]. In addition, there is expanding interest in moving beyond observing the dynamics of these processes to controlling those dynamics using ultrafast lasers (see, for example, Refs. [20,35,36]).

Despite the increasing attention devoted to these processes, so far most studies focused on a single molecular species and occurred under an assortment of experimental conditions. For example, the initiating ionization mechanism in previous bond rearrangement studies has variously included

single [8,11,37–42] and multiple photons [5,22,26,27,43] as well as electron [23,28,44] and heavy ion impact [2,7,30]. To assist in understanding these dynamics we examine bond rearrangement following ultrafast strong-field double ionization of three triatomic molecules: carbon dioxide, carbonyl sulfide, and water. It is hoped that this comparative study will provide baseline data that drives theoretical explorations of these processes.

To make a more meaningful cross-molecule comparison, we consider bond rearrangement in the context of the double-ionization branching ratio for each molecule, that is, the ratio of the bond rearrangement yield to the total yield of all the one-, two-, and three-body breakup channels following double ionization. This method of comparison [29,45–49] minimizes the effect of the different ionization potentials across the molecules since the different ionization potentials naturally lead to different rates of double ionization at the same laser intensity. To accurately obtain this ratio, all of the nonnegligible dissociative and nondissociative channels resulting from the ABC^{2+} parent must be evaluated.

As illustrated in Fig. 1, the three target molecules have different characteristics. CO_2 is linear and mass symmetric, OCS is linear but mass asymmetric, and water is bent and has a different highest occupied molecular orbital (HOMO) configuration than either CO_2 or OCS . The three neutral molecules have different ground-state vibrational frequencies for both stretching and bending modes (see Table I), and certainly have different vibrational frequencies for the associated molecular ions. A cross-molecule comparison can begin to probe how some of these factors might influence the bond rearrangement process. Since we perform an ion-ion coincidence measurement using a cold-target-recoil-ion-momentum-spectroscopy

*Present address: Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India.

†eric.wells@augie.edu

‡ibi@phys.ksu.edu

§tsevert@phys.ksu.edu

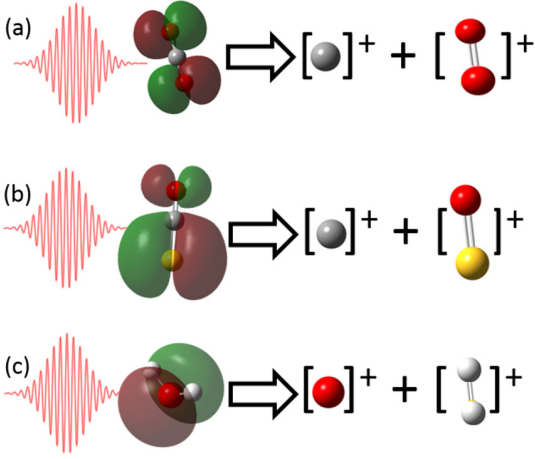


FIG. 1. The three molecules studied in this experiment along with the associated bond rearrangement channel. The HOMO of each target molecule is shown. (a) $\text{CO}_2 + n\omega \rightarrow \text{O}_2^+ + \text{C}^+$. (b) $\text{OCS} + n\omega \rightarrow \text{SO}^+ + \text{C}^+$. (c) $\text{D}_2\text{O} + n\omega \rightarrow \text{D}_2^+ + \text{O}^+$.

(COLTRIMS) [50,51] method, the data not only contain yields of the channels needed to calculate the branching ratio, but also the momentum vectors of the dissociating molecular fragments. From this three-dimensional data we evaluate the angular distributions and kinetic energy release (KER) distributions of the bond rearrangement process in the different molecules and also comment on previous strong-field measurements of bond rearrangements in CO_2 [26,27] and water [5,22,43,52].

Sections II and III describe the experimental method and data analysis procedures, respectively, that allow the accurate evaluation of the branching ratios in these targets despite the small overall magnitude of the bond rearrangement channel (around 0.1% order of magnitude in all cases) compared to other double-ionization channels. In Sec. IV we discuss overall trends in the branching ratio and some details of the measurements of each individual target. Our experiment indicates that the bond rearrangement branching ratio is highest in the water target. The difference in the bond rearrangement branching ratio between the three molecules is less than an order of magnitude.

II. EXPERIMENTAL METHOD

The laser pulses in this experiment have 23 fs (FWHM in intensity) pulse duration, a central wavelength of 790 nm, and

TABLE I. Vibrational frequencies for the stretching and bending modes of neutral CO_2 , D_2O , and OCS . Values are from NIST [53].

Molecule	Symmetric Stretch cm ⁻¹			Bend cm ⁻¹
CO ₂	1333			667
D ₂ O	2671			1178
	CO stretch cm ⁻¹	CS stretch cm ⁻¹		Bend cm ⁻¹
OCS	2062	859		520

TABLE II. Bond rearrangement branching ratios following double ionization of CO_2 , OCS , and D_2O . R includes all the channels listed in Tables III to V.

Molecular dissociation	Intensity (10^{14} W/cm^2)	R (%)
$\text{CO}_2^{2+} \rightarrow \text{O}_2^+ + \text{C}^+$	7.2 ± 1.3	0.0796 ± 0.0058
$\text{OCS}^{2+} \rightarrow \text{SO}^+ + \text{C}^+$	5.6 ± 0.8	0.0253 ± 0.0014
$\text{D}_2\text{O}^{2+} \rightarrow \text{D}_2^+ + \text{O}^+$	6.6 ± 1.0	0.199 ± 0.016

maximum pulse energy of 2 mJ. These pulses are produced at a 10-kHz repetition rate by a KMLabs ultrafast Ti:Sapphire chirped-pulse-amplification laser system known as PULSAR [54]. The laser pulse is characterized using second-harmonic-generation frequency-resolved-optical-gating (SHG-FROG) [55]. The peak laser intensity is determined by measuring the recoil momentum distribution of Ne^+ ions along the laser polarization and locating the point associated with the $2U_p$ kinetic energy of the electron [56], where U_p is the ponderomotive energy. At this point, rescattered electrons become more dominant than direct electrons in the above-threshold-ionization photoelectron spectrum. Intensities in these experiments were between 5.6 and $7.2 \times 10^{14} \text{ W/cm}^2$ as specified in Table II.

An $f = 7.5 \text{ cm}$ spherical mirror is used to focus the laser beam onto the supersonic molecular beam of a COLTRIMS [50,51] apparatus, from which all the charged products from the triatomic target are measured in coincidence by a time- and position-sensitive detector. The OCS gas was seeded into a helium buffer gas to cool the target and control the total count rate on the detector. On the other hand, the CO_2 and D_2O targets were not seeded in any buffer gas. The target molecules are randomly oriented with respect to the laser polarization in the supersonic molecular beam. The base pressure in the spectrometer region was below $2 \times 10^{-10} \text{ Torr}$, and the count rate on the detector was around 15 kHz, or approximately 1.5 ions per laser pulse. Since the charged fragments are recorded on an event-by-event basis, we can use momentum conservation in conjunction with the measured time and position of all the charged fragments to reconstruct the three-dimensional momentum distributions, as will be described below.

III. DATA ANALYSIS

In coincident molecular fragmentation studies, a standard way to describe the likelihood of a particular outcome is with a branching ratio [29,45–49,57,58]. (The branching ratio is sometimes called the “relative cross-section,” “abundance,” or “fragmentation pattern.”) We compute the branching ratio by dividing the yield of a specific coincidence channel by the sum of all possible products originating from a specific transient molecular ion such as ABC^{2+} . The branching ratio for bond rearrangement of a doubly charged triatomic molecule, i.e., ABC^{2+} going to $\text{AC}^+ + \text{B}^+$, is

$$R = \frac{M(\text{AC}^+ + \text{B}^+)}{\varepsilon \sum_i M(^{(1)}P_i) + \sum_j M(^{(2)}P_j) + \sum_k M(^{(3)}P_k)}, \quad (1)$$

where M stands for the measured counts in each channel after subtracting false coincidences (described below), $^{(1)}P$

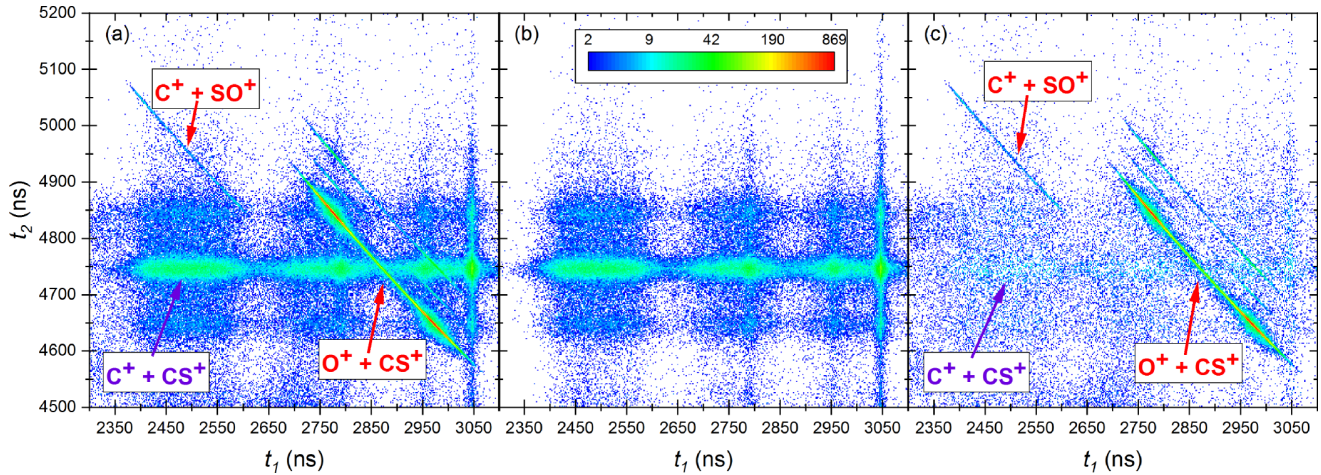


FIG. 2. A region of the CTOF data for the OCS measurement. (a) Measured data with the diagonal two-body breakup islands visible for several channels, including $C^+ + SO^+$ at the upper left. This bond rearrangement channel is clearly visible without any correction. An example false coincidence channel, $C^+ + CS^+$, is indicated with the purple arrow and text. (b) Simulated false coincidence spectrum. (c) The CTOF yield after subtraction of the scaled simulated false coincidence spectrum. Two-body breakup channels are identified. The main $^{12}C^{32}S^+ + O^+$ channel is accompanied by smaller satellite channels due to naturally occurring ^{13}C , ^{33}S , and ^{34}S isotopes. These channels are too small to be visible in the $C^+ + SO^+$ bond rearrangement channel.

denotes all channels with a final dicationic charge state where only single dicationic products were measured (including channels such as ABC^{2+} , $AB^{2+} + C$, and $A^{2+} + BC$), $^{(2)}P$ stands for all the two-body ion pair breakup channels (i.e., $AB^+ + C^+$, $B^+ + AC^+$, and $C^+ + AB^+$) and $^{(3)}P$ stands for all the three-body fragmentation channels where only the ion pairs are measured in coincidence (like $A^+ + B^+ + C$, $A^+ + B + C^+$ and $A + B^+ + C^+$). Note that the $^{(1)}P$ channels are multiplied by the detection efficiency, ε , to correct for the difference in detection efficiency of single ions (ε) with respect to ion pairs (ε^2), where we assumed the same detection efficiency for all ions.

The advantage of calculating the branching ratio with respect to all possible channels of the doubly ionized parent, as in Eq. (1), rather than the total yield of all measured ions is that when making a cross-molecule comparison, effects due to target dependent factors, such as the ionization potential, are minimized [29]. If, however, the population of the daughter dication changes with intensity, that can modify the branching ratio and make cross-molecule comparisons more complicated.

The goal of the data analysis is the extraction of the yields of the various $^{(1)}P$, $^{(2)}P$, and $^{(3)}P$ channels that are needed to calculate R . There are some complications to be addressed in this process: One factor is that due to nonuniform detection efficiency across the surface of the detector, we correct the yield for position-dependent losses on our detector using known symmetries about the laser polarization. Additional complicating factors we address are the presence of false coincidences, which affect the yields of $^{(2)}P$ and $^{(3)}P$, and the detection efficiency, which is needed to properly scale the $^{(1)}P$ yields and to subtract the contributions of higher charge states which affect the $^{(3)}P$ yield. The following paragraphs summarize how we address these points.

Since we are operating in the regime of ~ 1 ion per laser pulse, we have a significant contribution from false coinci-

dences, that is, coincident ions that arise from the fragmentation of two or more molecules in the same laser pulse. To reduce their effect on the calculated branching ratio, we generate the false coincident ion pairs by randomly pairing ions from different laser pulses [2,59–61]. Since we can generate an arbitrary number of random ion pairs, we identify a purely random feature in any spectrum and generate enough false coincidences to match it, so it is properly subtracted. For example, in Fig. 2 we show how to subtract randoms in the coincidence time-of-flight (CTOF) map for OCS. In particular, Fig. 2(a) shows the $SO^+ + C^+$ and $CS^+ + O^+$ channels, which appear as narrow diagonal stripes typical of two-body (i.e., momentum conserving) breakup of the parent molecule [62,63]. In addition, we also observe false coincidence structures, such as the $C^+ + CS^+$ false coincidence peak indicated by the purple arrow in Fig. 2(a). We scale the false coincidence distribution, shown in Fig. 2(b), to this purely random feature and subtract them to produce the “random free” spectrum shown in Fig. 2(c).

To analyze the two-body double-ionization breakup channels [$^{(2)}P$ contributions], we calculate the momenta of each fragment in the center-of-mass frame of the breakup (see, for example, Ref. [64]). To limit the contributions of other channels and other possible sources of contamination, we set gates on the laboratory frame momentum sum, i.e., the momentum distribution of the center of mass of the parent molecule.

To analyze the three-body breakup channels associated with double ionization [$^{(3)}P$ contributions], we select the apparent ion-pair coincidence channels containing an undetected third atomic fragment. Due to the high intensities of these measurements, the missing atom can either be neutral or charged. When the missing fragment is charged, we measure the complete three-body channel, scale it by the detection efficiency, and subtract it to reveal the three-body coincidence channel with a missing neutral fragment. To determine the

detection efficiency, we choose a three-body ion-pair coincidence channel where the features of channels due to a third missing neutral and charged fragment are clearly separated. The detection efficiency is then the scaling factor required to subtract the contributions associated with the missing charged fragment. For an example using a similar method for determining the detection efficiency using only two-body breakup, see Ref. [65]. Then, to calculate the momentum of the missing atom, we compute the initial laboratory-frame velocities of the measured ionic fragments and subtract the average initial center-of-mass velocity of the parent molecule, as determined from the coincidence channels where all fragments are measured. Using momentum conservation, we compute the momentum of the neutral atom.

Since momentum conservation is used to determine the momentum of the neutral fragment, it cannot also be used to compute the initial spread in the center-of-mass momentum due to the temperature of the molecular beam. Therefore, the momentum resolution is worse than the case of breakup channels where all fragments are measured. Fortunately, the increased uncertainty is minimal because the initial spread of the center-of-mass momentum, i.e., the temperature of the molecular beam, is low. For example, in the OCS measurement, the transverse temperature of the molecular beam was ~ 6 K while the longitudinal temperature was ~ 125 K. The temperatures were determined by examining the sum of momentum distributions in the laboratory frame. When determining the yield of each three-body channel with a neutral fragment, we correct for the competing isotopically substituted channels that cannot be separated using the isotopic abundance of each atom from the NIST database [66].

In analyzing the three-body channels, we neglect most charge asymmetric channels from the dication, like $O^{2+} + C + S$ in OCS, which are expected to have a lower rate than the charge symmetric channels [67,68]. The present OCS data supports this assumption, showing $CS^{2+} + O$ is less than 0.2% of the total double ionization yield, about an order of magnitude less than the smallest of the three-body channels containing two singly charged and one neutral fragment, $C^+ + O^+ + S$. Since we are mainly interested in the branching ratio of the bond rearrangement channels, the effect of the charge asymmetric channels is minimal because their yields only contribute to the denominator of Eq. (1).

Aside from statistical uncertainties, the primary contributions to the uncertainty in the evaluated branching ratio are due to the random coincidence subtraction and the corrections for position dependent losses.

IV. RESULTS AND DISCUSSION

The main result of this experiment is the branching ratio of the bond rearrangement channels from double ionization of CO_2 , OCS, and D_2O . These findings are summarized in Table II. There are two immediate conclusions that can be drawn from the results. First, bond rearrangement is more likely in D_2O than in CO_2 , which in turn is more likely than bond rearrangement in OCS. Second, all of the R values are within an order of magnitude.

Carbon dioxide has been described as a “showcase” [40] for the complexities involved in molecular fragmentation pro-

TABLE III. Branching ratios of the measured final products of doubly ionized CO_2 at $(7.2 \pm 1.3) \times 10^{14}$ W/cm². The $CO^+ + O^+$ channel contains contributions from both “prompt” and “dissociation in flight,” as discussed in the text.

Fragmentation Channel	R (%)
$CO^+ + O^+$	65.6 ± 4.5
$C^+ + O^+ + O$	23.7 ± 7.3
CO_2^{2+}	6.08 ± 0.81
$O^+ + O^+ + C$	4.6 ± 1.4
$C^+ + O_2^+$	0.0796 ± 0.0058

cesses. The intricacies in the fragmentation and isomerization of CO_2 can depend on the charge state of the ion [69–74], metastable states of the dication [75–78], the Renner-Teller effect [40,71], and the geometry of excited states [71,79]. As a result of these interesting features, CO_2 fragmentation has been examined using electron [77,80–83] and ion impact [84–86] as well as various photoionization studies [40,41,69–74,87,88].

Several of these studies noted the production of O_2^+ fragments [26,27,40,41], although we are not aware of any reports of the branching ratio. The results of our double ionization branching ratio measurement for CO_2 are reported in Table III.

Two recent strong-field studies of CO_2 report the observation of the $CO_2 + n\omega \rightarrow O_2^+ + C^+$ process induced with laser pulses centered near 800 nm [26,27]. While neither of these experiments reports an explicit branching ratio, Larimian *et al.* do point out that the yield of $O_2^+ + C^+$ is approximately three orders of magnitude lower than the $CO^+ + O^+$ channel [26]. Their estimate is consistent with our result, which was at nearly identical pulse duration but somewhat higher intensity: $(7.2 \pm 1.3) \times 10^{14}$ W/cm² in our measurement compared to 10^{14} W/cm² in their measurement [26].

There have been a number of previous studies of the fragmentation dynamics in OCS following strong-field multiple ionization [42,89–93], as well as similar studies using single photon [8,90,94–98], ion [99,100], and electron impact [101]. Many of these studies examined three-body breakup and did not focus on the bond rearrangement channel leading to SO^+ formation. Our results for the double ionization branching ratio in OCS are shown in Table IV. The strong preference for

TABLE IV. Branching ratios of the measured final products of doubly ionized OCS at $(5.6 \pm 0.8) \times 10^{14}$ W/cm².

Fragmentation channel	R (%)
OCS^{2+}	63.4 ± 6.2
$CO^+ + S^+$	26.8 ± 1.4
$C^+ + S^+ + O$	5.2 ± 1.3
$O^+ + S^+ + C$	1.55 ± 0.40
$C^+ + O^+ + S$	1.49 ± 0.38
$CS^+ + O^+$	1.358 ± 0.072
$CS^{2+} + O$	0.159 ± 0.015
$SO^+ + C^+$	0.0253 ± 0.0014

TABLE V. Branching ratios of the measured final products of doubly ionized D_2O at $(6.6 \pm 1.0) \times 10^{14} \text{ W/cm}^2$. As noted in the text, the absence of the D_2O^{2+} channel is expected from the details of the potential energy surface of the ground electronic state of D_2O^{2+} .

Fragmentation channel	R (%)
$D^+ + DO^+$	74.6 ± 5.0
$D^+ + O^+ + D$	22.1 ± 6.8
$D^+ + D^+ + O$	3.10 ± 0.95
$D_2^+ + O^+$	0.199 ± 0.016

$CO^+ + S^+$ over $CS^+ + O^+$ has been ascribed to the fact that the C-O bond is stronger than the C-S bond in OCS^{2+} [39,97]. Here we note that the two-body $CS^+ + O^+$ channel is even smaller than the three-body channels. We are not aware of any previous measurements of the double ionization branching ratio that include the $SO^+ + C^+$ channel.

Bond rearrangement in water has been the subject of a variety of studies using ion [30,102,103] and electron [44] impact as well as single [11,37,38,42] and multiple photon absorption [5,22,43,52]. Oxygen core excitation via synchrotron radiation [11,37,38,42] suggests that the stimulation of bending motion, or a combination of bending and symmetric stretch modes, enhances the production of H_2^+ . The process leading to the formation of H_2^+ is thought to be rapid in these situations, as short as 10 fs on the dication surface [11,42]. While fast ion impact predominantly interacts with valence, rather than core, electrons, the bond rearrangement process appears to be explained by a rapid process in these cases as well, specifically a vertical ionization to the dication leading to a small probability of reaching the $H_2^+ + O^+$ dissociation limit [2,30,44].

When water is ionized by very short laser pulses (5–10 fs), bond rearrangement has been reported to occur in several measurements [5,22,43]. Recent measurements by McCracken *et al.* [52], in contrast, reported no evidence of bond rearrangement in D_2O when ionized by 40-fs, 800-nm pulses. We observe $D_2O^{2+} \rightarrow D_2^+ + O^+$ bond rearrangement at a pulse duration of 23 fs, in between the shorter [5,22] and longer [52] pulses used in earlier experiments. As reported in Table II, R for water is larger than for CO_2 or OCS . The detailed analysis of the D_2O fragmentation, presented in Table V, shows that there is no yield in the main $(^1)P$ channel (i.e., D_2O^{2+}). This is expected because the potential well of the ground electronic state of the water dication is shallow, supporting states with lifetime around 1 ps or smaller [104]. In addition, there may be small amounts of contamination in the $D^+ + D^+ + O$ and $D^+ + O^+ + D$ channels. We estimate that the contamination should have a negligible effect on the branching ratio of $D_2^+ + O^+$, which is the main channel of interest.

A theme throughout previous studies of bond rearrangement [8,11,14,22,23,26–28,39–42] has been that the primary initiating step is the stimulation of bending modes in the triatomic molecule. With this background, it is not surprising that the bent water molecule has the highest bond rearrangement branching ratio of the molecules examined in this study. In addition to the favorable configuration of the neutral target,

the lighter mass of the deuterium atoms in D_2O can lead to larger vibrational amplitude than for oxygen or sulfur in CO_2 and OCS , respectively, meaning that a vertical projection of the neutral vibrational wave function onto the dication potential energy surface(s) will sample extensive parts of the surface(s), leading to the possibility of a greater range of dissociation outcomes. This qualitative argument can also explain why SO^+ is less likely to form from OCS than O_2^+ is from CO_2 , since the sulfur atom is double the oxygen mass. Similar isotopic trends were observed in studies of bond rearrangement in methane, ammonia and water [7,30].

The above discussion assumes a vertical transition from the neutral to the dication potential energy surface. Note, however, that since we are studying bond rearrangement in a strong laser field, it is possible for the double ionization to occur in two steps. Specifically, once the molecule is singly ionized, the wave packet can evolve on the cation potential energy surfaces for a short time within the duration of the laser pulse before the molecule is further ionized, a dominant mechanism in many dissociative ionization cases (see, e.g., the review by Codling and Frasinski [105]). However, the relative importance of this mechanism in bond rearrangement is an open question because of the need for significant change in the nuclear geometry during the laser pulse. Such a “two-step” ionization mechanism was invoked by Larimian *et al.* [26] for O_2^+ formation from CO_2 , which is described in more detail later in this article. Even during stepwise ionization, however, the wave packets associated with lighter fragments can evolve more rapidly on the cation surfaces, allowing more favorable bond rearrangement geometries to be reached before the laser pulse initiates the second ionization step. Since our measurement cannot distinguish direct versus stepwise double ionization, we can not exclude either possibility. To explore the role of intermediate cationic states, it may help to perform Fourier transform vibrational spectroscopy measurements using a strong-field femtosecond pump-probe scheme [26,106,107].

In addition, while the simple vertical ionization explanation above describes the trends in the branching ratio across the molecules, a comparison of the angular distributions of the bond rearrangement channels gives indications of more complex dynamics. Figures 3 and 4 show the angular distributions of the bond rearrangement channels in OCS and D_2O , respectively. In both of these molecules, the bond rearrangement fragment tends to be ejected along the laser polarization direction. Several previous studies [22,39,43] described particular mechanisms, specific to each molecule, that explain this aligned dissociation.

As a heteronuclear, nonsymmetric, linear, polar molecule, OCS has been a standard molecule for studies of alignment-dependent ionization, e.g., Refs. [108–111]. Double ionization of OCS leading to OCS^{2+} at $2 \times 10^{14} \text{ W/cm}^2$ is minimized for $\cos \theta = \pm 1$ [111], although the main two-body dissociative $CO^+ + S^+$ channel is peaked at $\cos \theta = \pm 1$. Both the dissociative and nondissociative distributions are thought to become less sharply peaked as the laser intensity increases and more dication states are accessible [111]. Our observation, shown in Fig. 3, is that the bond rearrangement ($SO^+ + C^+$) angular distribution follows the same trend as the main dissociative double ionization channel ($CO^+ + S^+$).

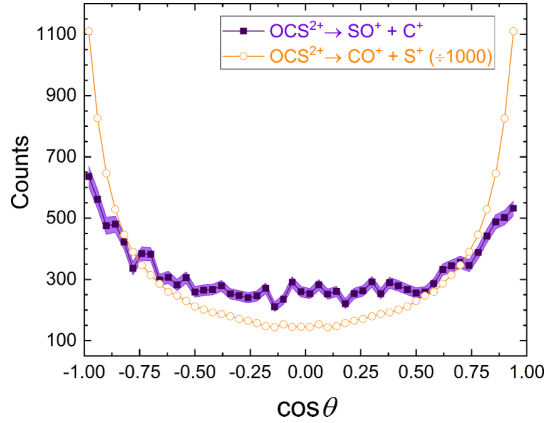


FIG. 3. The angular distribution of the $\text{OCS}^{2+} \rightarrow \text{SO}^+ + \text{C}^+$ bond rearrangement channel (solid purple squares) and the main two-body fragmentation channel $\text{OCS}^{2+} \rightarrow \text{CO}^+ + \text{S}^+$ (open orange circles). Here θ is the angle between the laser polarization and the direction of the lighter fragment of the ion-pair. The shaded regions indicate the uncertainty in the measurements and are small for the $\text{OCS}^{2+} \rightarrow \text{CO}^+ + \text{S}^+$ channel.

While the ground-state configuration of the neutral OCS molecule is linear, the minimum energy configuration of the dication is bent [112], with an energetic barrier of about 4 eV separating the linear and nonlinear configurations. Brites *et al.* [39] performed calculations that show that at an OCS angle of about 150° , the OCS^{2+} undergoes isomerization from OCS^{2+} to CSO^{2+} . In other words, in this process the oxygen atom migrates to the other side of the molecule. Brites *et al.* further predicted that the lowest electronic state of the CSO^{2+} isomer is repulsive, leading to dissociation into $\text{C}^+ + \text{SO}^+$ reaction products, as observed by Sorensen *et al.* [8,42]. This process increases when driven by resonant excitation of the $\text{C } 1s \rightarrow \pi^*$ transition that induces a bending mode which is

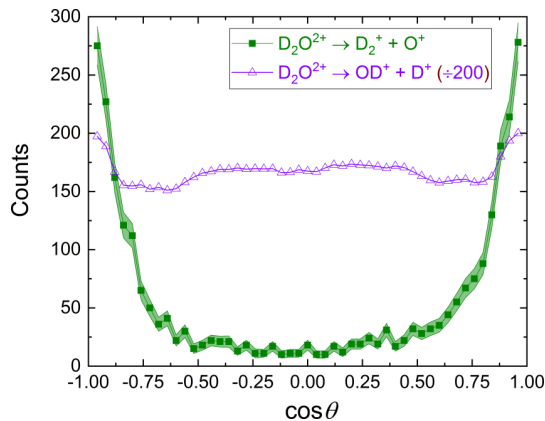


FIG. 4. The angular distribution of the $\text{D}_2\text{O}^{2+} \rightarrow \text{D}_2^+ + \text{O}^+$ (filled green squares) and $\text{D}_2\text{O}^{2+} \rightarrow \text{OD}^+ + \text{D}^+$ (open violet triangles) channels where θ is the angle between the laser polarization and the direction of the least massive fragment in the respective ion-pair. The shaded regions indicate the uncertainty in the measurements. The small decrease in the $\text{OD}^+ + \text{D}^+$ distribution around $\cos \theta = 0$ is likely due to a small fraction of D^+ fragments missing the detector.

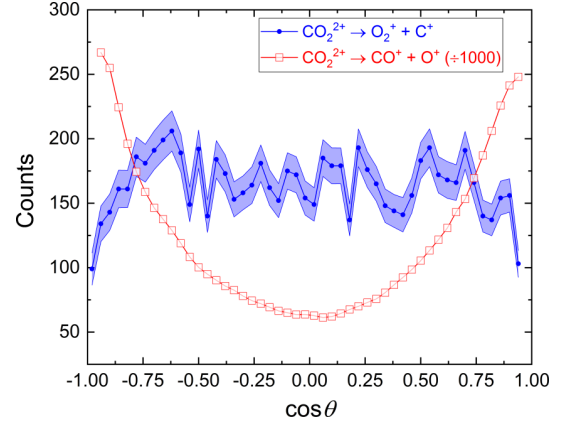


FIG. 5. The angular distribution of the $\text{CO}_2^{2+} \rightarrow \text{O}_2^+ + \text{C}^+$ (solid blue circles) and $\text{CO}_2^{2+} \rightarrow \text{CO}^+ + \text{O}^+$ (open red squares) where θ is the angle between the laser polarization and the direction of the lighter dissociating fragment in each ion-pair. The shaded regions indicate the uncertainty in the measurements. The dips near $\cos \theta = \pm 1$ are due to reduced detection efficiency near the center of the detector.

further enhanced by the Renner-Teller effect [8]. This mechanism is triggered if the photoabsorption induces a bending mode with the transition dipole aligned with the polarization direction [8].

If inducing a bending mode that eventually leads to isomerization reaching a dissociative CSO^{2+} state is also the primary driver of $\text{SO}^+ + \text{C}^+$ production in strong-field ionization (the previous work [8,39,42,112] involved single photons), then one would expect a similar alignment when the process is initiated with a linearly polarized laser pulse. Indeed, our measured angular distribution is peaked along the polarization direction, similar to the single photon data [8]. The peak of our measured KER distribution is located at approximately 5.5 eV, 1.5 eV higher than the value predicted by Brites *et al.* [39] for dissociation of the lowest electronic state of the CSO^{2+} into $\text{SO}^+ + \text{C}^+$, showing that there are differences between the single-photon and strong-field measurements despite the similarities of the fragment angular distributions. Additional theoretical efforts are needed to develop further insight into the strong-field dynamics.

Like the OCS results, our measured $\text{D}_2^+ + \text{O}^+$ angular distribution, shown in Fig. 4, is peaked along the laser polarization direction. In contrast, the main $\text{OD}^+ + \text{D}^+$ fragmentation channel has a much less aligned distribution. Thus we conclude that the angular distribution of the bond rearrangement channels is not generally the same as the predominant double-ionization channel. Mathur *et al.* [22] examined the dynamics of the bond rearrangement process using velocity map imaging after ionization by 10-fs, 790-nm laser pulses. Our measured angular distributions, shown in Fig. 4, are consistent with the shorter pulse measurement [22], with both showing that $\text{D}_2^+ + \text{O}^+$ fragment ejection is strongly peaked along the laser polarization.

While the OCS and D_2O bond rearrangement channels are aligned along the laser polarization, the angular distribution for $\text{CO}_2^{2+} \rightarrow \text{O}_2^+ + \text{C}^+$ shown in Fig. 5 is isotropic, at least within the uncertainty of our measurement. The angular

distribution of the bond rearrangement channels is also different than the angular distribution of the dominant double ionization channel, $\text{CO}_2^{2+} \rightarrow \text{CO}^+ + \text{O}^+$, which, as shown in Fig. 5, is strongly peaked along the laser polarization direction. These differences can originate from the angular dependence of the ionization process. Previous measurements of single- and double-ionization of CO_2 have shown that the ionization is peaked for different angles between the laser polarization and the molecular axis depending on the final state of the (di)cation [106,113,114]. For example, $\text{CO}_2^{2+} \rightarrow \text{CO}^+ + \text{O}^+$ is peaked for ionization parallel to the polarization [106], while the ionization is peaked perpendicular and at 45° to the polarization for other final states [106,113,114]. If a number of these CO_2^{2+} states lead to bond rearrangement, then the resulting angular distribution from the combination could be approximately isotropic.

Another possible explanation of the isotropic angular distribution for $\text{CO}_2^{2+} \rightarrow \text{O}_2^+ + \text{C}^+$ shown in Fig. 5 are the dynamics of the bond rearrangement process. Based on their COLTRIMS measurements, associated calculations and further pump-probe measurements, Larimian *et al.* [26] hypothesized that O_2^+ formation occurs after the nuclear wave packet evolves on the CO_2^+ potential energy surface toward a bent configuration, which they estimate to occur within 25 fs. In their model, subsequent ionization to a CO_2^{2+} surface with a triangular configuration initiates the ejection of the carbon atom.

One possible explanation of the isotropic angular distribution for the $\text{O}_2^+ + \text{C}^+$ bond rearrangement channel is that there is a delay, after the rapid formation of the triangular dicationic CO_2^{2+} states within the laser pulse duration, that “erases” any angular dependence of the initial step(s) in the bond rearrangement process. If this is the case, the lifetime of the dication would need to be longer than the rotational period of CO_2^{2+} but shorter than ~ 150 ns. Longer lifetimes would be detected as dissociation in flight (see, for example Ref. [115]). The lower limit set by the rotational period is ≈ 33 ps for the $J = 1$ state for each of the $X^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$ electronic states of CO_2^{2+} , which we estimated using the spectroscopic constants reported in Ref. [116]. The upper limit is estimated by modeling our experimental conditions to determine when prompt breakup, i.e., events that do not significantly move in the spectrometer before dissociating, is separated from dissociation in flight. Note neither our data nor that of Long *et al.* [27] show any evidence of dissociation in flight of the $\text{O}_2^+ + \text{C}^+$ bond rearrangement channel.

On the other hand, a fraction of events of CO_2^{2+} breakup into $\text{CO}^+ + \text{O}^+$ are known to dissociate in flight [27,75], where Field and Eland reported a mean lifetime of 900 ns of the intermediate metastable CO_2^{2+} [75]. The angular distribution of the $\text{CO}^+ + \text{O}^+$ presented in Fig. 5 focuses on the prompt dissociation, which is observed to be aligned along the laser polarization, in contrast to the $\text{O}_2^+ + \text{C}^+$ bond rearrangement channel which is isotropic.

While the branching ratio for bond rearrangement processes in polyatomic molecules such as ammonia and methane [7] can vary over orders of magnitude (e.g., the large $\text{H}_2^+ + \text{CH}_2^+$ channel in methane), it is curious to note the relatively similar branching ratios for the triatomic molecules examined here. Despite the differences in the structure and bonding of

the molecules, and the observed differences in the angular distributions of the bond rearrangement fragments discussed above, the bond rearrangement branching ratios in double ionization are all within an order of magnitude of each other. This is consistent with previous measurements of similar branching ratios in water [30] and even acetylene [28], where the $\text{H}_2^+ + \text{C}_2^+$ channel was estimated to be 0.05% of the dominant ion-pair channel $\text{H}^+ + \text{C}_2\text{H}^+$. Theoretical treatment may reveal if the similarity in the branching ratios is just a coincidence or if there is a general predisposition for bond rearrangement involving two atoms located at the edges of a small molecule to occur at this level.

V. SUMMARY

The strong-field induced bond rearrangement branching ratio of three doubly ionized triatomic molecules (CO_2 , OCS , and D_2O) was measured to provide comparative information about the bond rearrangement process in which the two edge atoms break from the center atom and reform into a diatomic ion. Out of these triatomic molecules, bond rearrangement occurs most often in water, which has an initially bent geometry and the least massive edge atoms. The mass-dependent trend extends to CO_2 and OCS , where the more massive sulfur atom on the edge of the OCS molecule can qualitatively explain the lower bond rearrangement branching ratio in OCS compared to CO_2 .

Both D_2O and OCS are more likely to undergo bond rearrangement that ejects the newly formed molecular ion along the laser polarization, which is consistent with previous explanations of these processes [8,22,39,42]. Bond rearrangement in CO_2 , in contrast, leads to a nearly isotropic distribution of the $\text{O}_2^+ + \text{C}^+$ breakup. Furthermore, OCS was the only molecule in which the bond rearrangement channel had an angular distribution that was similar to the main dissociative double ionization channel. Thus it appears that the details of the bond rearrangement mechanisms are different in the molecules studied here.

Despite these differences between CO_2 , OCS , and D_2O , however, the double ionization bond rearrangement branching ratios are similar in the three molecules. This similarity is somewhat curious since the differences are much less than observed in similar measurements of slightly larger polyatomic molecules [7]. An increased theoretical understanding of these processes is necessary to determine if the similarities are a product of some general behavior of bond rearrangement in triatomic molecules.

ACKNOWLEDGMENTS

We thank Charles Fehrenbach for assistance with the PULSAR laser. S.Z. thanks the organizers of the Kansas State University Physics Department Research Experience for Undergraduates program for including him in their activities. J.H. acknowledges support by the National Science Foundation (NSF) through NSF Grant No. PHYS-175777. Augustana University personnel are funded by NSF Grant No. PHY-1723002. This project is supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science,

US Department of Energy via its support for JRML under Grant No. DE-FG02-86ER13491. E.W. received partial sabbatical leave support and S.Z. received funding for

summer housing and local expenses from the same DOE grant. The PULSAR laser was provided by Grant No. DE-FG02-09ER16115 from the same funding agency.

- [1] Y. Furukawa, K. Hoshina, K. Yamanouchi, and H. Nakano, *Chem. Phys. Lett.* **414**, 117 (2005).
- [2] I. Ben-Itzhak, A. M. Sayler, M. Leonard, J. Maseberg, D. Hathiramani, E. Wells, M. Smith, J. Xia, P. Wang, K. Carnes, and B. Esry, *Nucl. Instrum. Methods Phys. Res., Sect. B* **233**, 284 (2005).
- [3] T. Okino, Y. Furukawa, P. Liu, T. Ichikawa, R. Itakura, K. Hoshina, K. Yamanouchi, and H. Nakano, *J. Phys. B* **39**, S515 (2006).
- [4] K. Hoshina, Y. Furukawa, T. Okino, and K. Yamanouchi, *J. Chem. Phys.* **129**, 104302 (2008).
- [5] F. A. Rajgara, A. K. Dharmadhikari, D. Mathur, and C. P. Safvan, *J. Chem. Phys.* **130**, 231104 (2009).
- [6] S. Kazianis, I. Lontos, G. Karras, C. Corsi, M. Bellini, and C. Kosmidis, *J. Chem. Phys.* **131**, 144308 (2009).
- [7] B. Jochim, A. Lueking, L. Doshier, S. Carey, E. Wells, E. Parke, M. Leonard, K. D. Carnes, and I. Ben-Itzhak, *J. Phys. B* **42**, 091002 (2009).
- [8] J. Laksman, D. Céolin, M. Gisselbrecht, and S. L. Sorensen, *J. Chem. Phys.* **133**, 144314 (2010).
- [9] K. Hoshina, H. Kawamura, M. Tsuge, M. Tamiya, and M. Ishiguro, *J. Chem. Phys.* **134**, 064324 (2011).
- [10] P. M. Kraus, M. C. Schwarzer, N. Schirmel, G. Urbasch, G. Frenking, and K.-M. Weitzel, *J. Chem. Phys.* **134**, 114302 (2011).
- [11] J. Laksman, E. P. Månsson, A. Sankari, D. Céolin, M. Gisselbrecht, and S. L. Sorensen, *Phys. Chem. Chem. Phys.* **15**, 19322 (2013).
- [12] K. Nakai, T. Kato, H. Kono, and K. Yamanouchi, *J. Chem. Phys.* **139**, 181103 (2013).
- [13] R. Fernando, A. Dey, B. M. Broderick, B. Fu, Z. Homayoon, J. M. Bowman, and A. G. Suits, *J. Phys. Chem. A* **119**, 7163 (2014).
- [14] B. Wei, Y. Zhang, X. Wang, D. Lu, G. C. Lu, B. H. Zhang, Y. J. Tang, R. Hutton, and Y. Zou, *J. Chem. Phys.* **140**, 124303 (2014).
- [15] H. Ibrahim, B. Wales, S. Beaulieu, B. E. Schmidt, N. Thiré, E. P. Fowe, É. Bisson, C. T. Hebeisen, V. Wanie, M. Giguère, J.-C. Kieffer, M. Spanner, A. D. Bandrauk, J. Sanderson, M. S. Schuurman, and F. Légaré, *Nat. Commun.* **5**, 4422 (2014).
- [16] C. E. Liekhus-Schmaltz, I. Tenney, T. Osipov, A. Sanchez-Gonzalez, N. Berrah, R. Boll, C. Bomme, C. Bostedt, J. D. Bozek, S. Carron, R. Coffee, J. Devin, B. Erk, K. R. Ferguson, R. W. Field, L. Foucar, L. J. Frasinski, J. M. Glowina, M. Gühr, A. Kamalov, J. Krzywinski, H. Li, J. P. Marangos, T. J. Martinez, B. K. McFarland, S. Miyabe, B. Murphy, A. Natan, D. Rolles, A. Rudenko, M. Siano, E. R. Simpson, L. Spector, M. Swiggers, D. Walke, S. Wang, T. Weber, P. H. Bucksbaum, and V. S. Petrovic, *Nat. Commun.* **6**, 8199 (2015).
- [17] S. Maeda, T. Taketsugu, K. Ohno, and K. Morokuma, *J. Am. Chem. Soc.* **137**, 3433 (2015).
- [18] H. Wu, S. Zhang, J. Zhang, Y. Yang, L. Deng, T. Jia, Z. Wang, and Z. Sun, *J. Phys. Chem. A* **119**, 2052 (2015).
- [19] P. L. Houston, R. Conte, and J. M. Bowman, *J. Phys. Chem. A* **120**, 5103 (2016).
- [20] M. Kübel, R. Siemering, C. Burger, N. G. Kling, H. Li, A. S. Alnaser, B. Bergues, S. Zherebtsov, A. M. Azzeer, I. Ben-Itzhak, R. Moshhammer, R. de Vivie-Riedle, and M. F. Kling, *Phys. Rev. Lett.* **116**, 193001 (2016).
- [21] J. A. DeVine, M. L. Weichman, X. Zhou, J. Ma, B. Jiang, H. Guo, and D. M. Neumark, *J. Am. Chem. Soc.* **138**, 16417 (2016).
- [22] D. Mathur, A. K. Dharmadhikari, J. A. Dharmadhikari, and P. Vasa, *J. Phys. B* **50**, 154004 (2017).
- [23] P. Bhatt, T. Sairam, A. Kumar, H. Kumar, and C. P. Safvan, *Phys. Rev. A* **96**, 022710 (2017).
- [24] N. Ekanayake, M. Nairat, B. Kaderiya, P. Feizollah, B. Jochim, T. Severt, B. Berry, K. R. Pandiri, K. D. Carnes, S. Pathak, D. Rolles, A. Rudenko, I. Ben-Itzhak, C. A. Mancuso, B. S. Fales, J. E. Jackson, B. G. Levine, and M. Dantus, *Sci. Rep.* **7**, 4703 (2017).
- [25] J. A. DeVine, M. L. Weichman, B. Laws, J. Chang, M. C. Babin, G. Balardi, C. Xie, C. L. Malbon, W. C. Lineberger, D. R. Yarkony, R. W. Field, S. T. Gibson, J. Ma, H. Guo, and D. M. Neumark, *Science* **358**, 336 (2017).
- [26] S. Larimian, S. Erattupuzha, S. Mai, P. Marquetand, L. González, A. Baltuška, M. Kitzler, and X. Xie, *Phys. Rev. A* **95**, 011404(R) (2017).
- [27] J. Long, F. J. Furch, J. Durá, A. S. Tremsin, J. Vallerger, C. P. Schulz, A. Rouzée, and M. J. J. Vrakking, *J. Chem. Phys.* **147**, 013919 (2017).
- [28] S. Xu, H. Zhao, X. Zhu, D. Guo, W. Feng, K.-C. Lau, and X. Ma, *Phys. Chem. Chem. Phys.* **20**, 27725 (2018).
- [29] N. Ekanayake, T. Severt, M. Nairat, N. P. Weingartz, B. M. Farris, B. Kaderiya, P. Feizollah, B. Jochim, F. Ziaee, K. Borne, K. Raju P., K. D. Carnes, D. Rolles, A. Rudenko, B. G. Levine, J. E. Jackson, I. Ben-Itzhak, and M. Dantus, *Nat. Commun.* **9**, 5186 (2018).
- [30] M. Leonard, A. M. Sayler, K. D. Carnes, E. M. Kaufman, E. Wells, R. Cabrera-Trujillo, B. D. Esry, and I. Ben-Itzhak, *Phys. Rev. A* **99**, 012704 (2019).
- [31] H. B. Gray, *Nat. Chem.* **1**, 7 (2009).
- [32] M. P. Grubb, M. L. Warter, A. G. Suits, and S. W. North, *J. Phys. Chem. Lett.* **1**, 2455 (2010).
- [33] M. P. Grubb, M. L. Warter, H. Xiao, S. Maeda, K. Morokuma, and S. W. North, *Science* **335**, 1075 (2012).
- [34] Z. Lu, Y. C. Chang, Q.-Z. Yin, C. Y. Ng, and W. M. Jackson, *Science* **346**, 61 (2014).
- [35] N. Schirmel, N. Reusch, P. Horsch, and K.-M. Weitzel, *Faraday Discuss.* **163**, 461 (2013).
- [36] E. Wells, C. Rallis, M. Zohrabi, R. Siemering, B. Jochim, P. Andrews, U. Ablikim, B. Gaire, S. De, K. Carnes, B. Bergues, R. de Vivie-Riedle, M. Kling, and I. Ben-Itzhak, *Nat. Commun.* **4**, 2895 (2013).
- [37] M. N. Piancastelli, A. Hempelmann, F. Heiser, O. Gessner, A. Rüdél, and U. Becker, *Phys. Rev. A* **59**, 300 (1999).

- [38] A. Hiraya, K. Nobusada, M. Simon, K. Okada, T. Tokushima, Y. Senba, H. Yoshida, K. Kamimori, H. Okumura, Y. Shimizu, A.-L. Thomas, P. Millie, I. Koyano, and K. Ueda, *Phys. Rev. A* **63**, 042705 (2001).
- [39] V. Brites, J. Eland, and M. Hochlaf, *Chem. Phys.* **346**, 23 (2008).
- [40] J. Laksman, E. P. Månsson, C. Grunewald, A. Sankari, M. Gisselbrecht, D. Céolin, and S. L. Sorensen, *J. Chem. Phys.* **136**, 104303 (2012).
- [41] J. H. D. Eland, S. Zagorodskikh, R. J. Squibb, M. Mucke, S. L. Sorensen, and R. Feifel, *J. Chem. Phys.* **140**, 184305 (2014).
- [42] S. L. Sorensen, M. Gisselbrecht, J. Laksman, E. P. Månsson, D. Céolin, A. Sankari, and F. Afaneh, *J. Phys.: Conf. Ser.* **488**, 012006 (2014).
- [43] M. Garg, A. K. Tiwari, and D. Mathur, *J. Chem. Phys.* **136**, 024320 (2012).
- [44] H. C. Straub, B. G. Lindsay, K. A. Smith, and R. F. Stebbings, *J. Chem. Phys.* **108**, 109 (1998).
- [45] B. Brehm, J. Eland, R. Frey, and H. Schulte, *Int. J. Mass Spectrom. Ion Phys.* **21**, 373 (1976).
- [46] K. Wohrer, G. Sampoll, R. L. Watson, M. Chabot, O. Heber, and V. Horvat, *Phys. Rev. A* **46**, 3929 (1992).
- [47] D. Mathur, *Phys. Rep.* **225**, 193 (1993).
- [48] I. Ben-Itzhak, K. D. Carnes, S. G. Ginther, D. T. Johnson, P. J. Norris, and O. L. Weaver, *Phys. Rev. A* **47**, 3748 (1993).
- [49] E. Wells, V. Krishnamurthi, K. D. Carnes, N. G. Johnson, H. D. Baxter, D. Moore, K. M. Bloom, B. M. Barnes, H. Tawara, and I. Ben-Itzhak, *Phys. Rev. A* **72**, 022726 (2005).
- [50] J. Ullrich, R. Moshhammer, R. Dörner, O. Jagutzki, V. Mergel, H. Schmidt-Böcking, and L. Spielberger, *J. Phys. B* **30**, 2917 (1997).
- [51] J. Ullrich, R. Moshhammer, A. Dorn, R. Dörner, L. P. H. Schmidt, and H. Schmidt-Böcking, *Rep. Prog. Phys.* **66**, 1463 (2003).
- [52] G. A. McCracken, A. Kaldun, C. Liekhus-Schmaltz, and P. H. Bucksbaum, *J. Chem. Phys.* **147**, 124308 (2017).
- [53] T. Shimanouchi, *Tables of Molecular Vibrational Frequencies Consolidated Volume I*, Vol. I (National Bureau of Standards, Gaithersburg, MD, 1972).
- [54] X. Ren, A. M. Summers, K. Raju P., A. Vajdi, V. Makhija, C. W. Fehrenbach, N. G. Kling, K. J. Betsch, Z. Wang, M. F. Kling, K. D. Carnes, I. Ben-Itzhak, C. Trallero-Herrero, and V. Kumarappan, *J. Opt.* **19**, 124017 (2017).
- [55] R. Trebino, K. W. DeLong, D. N. Fittinghoff, J. N. Sweetser, M. A. Krumbügel, B. A. Richman, and D. J. Kane, *Rev. Sci. Instrum.* **68**, 3277 (1997).
- [56] V. L. B. de Jesus, B. Feuerstein, K. Zrost, D. Fischer, A. Rudenko, F. Afaneh, C. D. Schröter, R. Moshhammer, and J. Ullrich, *J. Phys. B* **37**, L161 (2004).
- [57] A. J. R. Heck and D. W. Chandler, *Annu. Rev. Phys. Chem.* **46**, 335 (1995).
- [58] R. E. Continetti, *Annu. Rev. Phys. Chem.* **52**, 165 (2001).
- [59] A. E. Slattery, T. A. Field, M. Ahmad, R. I. Hall, P. Lablanquie, and F. Penent, *Meas. Sci. Technol.* **13**, 2007 (2002).
- [60] G. F. Knoll, *Radiation Detection and Measurement* (John Wiley and Sons Ltd., New York, 2010).
- [61] X. Gong, Q. Song, Q. Ji, K. Lin, H. Pan, J. Ding, H. Zeng, and J. Wu, *Phys. Rev. Lett.* **114**, 163001 (2015).
- [62] J. Eland, F. Wort, and R. Royds, *J. Electron Spectrosc. Relat. Phenom.* **41**, 297 (1986).
- [63] I. Ben-Itzhak, S. Ginther, and K. Carnes, *Nucl. Instrum. Methods Phys. Res., Sect. B* **66**, 401 (1992).
- [64] T. Jahnke, T. Weber, T. Osipov, A. Landers, O. Jagutzki, L. Schmidt, C. Cocke, M. Prior, H. Schmidt-Böcking, and R. Dörner, *J. Electron Spectrosc. Relat. Phenom.* **141**, 229 (2004), Frontiers of Coincidence Experiments.
- [65] B. Gaire, A. M. Sayler, P. Q. Wang, N. G. Johnson, M. Leonard, E. Parke, K. D. Carnes, and I. Ben-Itzhak, *Rev. Sci. Instrum.* **78**, 024503 (2007).
- [66] M. Berglund and M. E. Wieser, *Pure Appl. Chem.* **83**, 397 (2011).
- [67] N. G. Kling, J. McKenna, A. M. Sayler, B. Gaire, M. Zohrabi, U. Ablikim, K. D. Carnes, and I. Ben-Itzhak, *Phys. Rev. A* **87**, 013418 (2013).
- [68] W. Lai and C. Guo, *Phys. Rev. A* **92**, 013402 (2015).
- [69] T. Masuoka, *Phys. Rev. A* **50**, 3886 (1994).
- [70] G. Ohrwall, M. M. S. Anna, W. C. Stolte, I. Dominguez-Lopez, L. T. N. Dang, A. S. Schlachter, and D. W. Lindle, *J. Phys. B* **35**, 4543 (2002).
- [71] Y. Muramatsu, K. Ueda, N. Saito, H. Chiba, M. Lavollée, A. Czasch, T. Weber, O. Jagutzki, H. Schmidt-Böcking, R. Moshhammer, U. Becker, K. Kubozuka, and I. Koyano, *Phys. Rev. Lett.* **88**, 133002 (2002).
- [72] Z. D. Pešić, D. Rolles, R. C. Bilodeau, I. Dimitriu, and N. Berrah, *Phys. Rev. A* **78**, 051401(R) (2008).
- [73] R. K. Kushawaha, S. S. Kumar, I. A. Prajapati, K. P. Subramanian, and B. Bapat, *J. Phys. B* **42**, 105201 (2009).
- [74] J. H. D. Eland, L. Andric, P. Linusson, L. Hedin, S. Plogmaker, J. Palaudoux, F. Penent, P. Lablanquie, and R. Feifel, *J. Chem. Phys.* **135**, 134309 (2011).
- [75] T. A. Field and J. H. Eland, *Chem. Phys. Lett.* **211**, 436 (1993).
- [76] A. E. Slattery, T. A. Field, M. Ahmad, R. I. Hall, J. Lambourne, F. Penent, P. Lablanquie, and J. H. D. Eland, *J. Chem. Phys.* **122**, 084317 (2005).
- [77] V. Sharma, B. Bapat, J. Mondal, M. Hochlaf, K. Giri, and N. Sathyamurthy, *J. Phys. Chem. A* **111**, 10205 (2007).
- [78] Y. Hikosaka, Y. Shibata, K. Soejima, H. Iwayama, and E. Shigemasa, *Chem. Phys. Lett.* **603**, 46 (2014).
- [79] K. Ueda and J. H. D. Eland, *J. Phys. B* **38**, S839 (2005).
- [80] C. Tian and C. R. Vidal, *Phys. Rev. A* **58**, 3783 (1998).
- [81] B. Bapat and V. Sharma, *J. Phys. B* **40**, 13 (2006).
- [82] X. Wang, Y. Zhang, D. Lu, G. C. Lu, B. Wei, B. H. Zhang, Y. J. Tang, R. Hutton, and Y. Zou, *Phys. Rev. A* **90**, 062705 (2014).
- [83] E. Wang, X. Shan, Z. Shen, M. Gong, Y. Tang, Y. Pan, K.-C. Lau, and X. Chen, *Phys. Rev. A* **91**, 052711 (2015).
- [84] N. Neumann, D. Hant, L. P. H. Schmidt, J. Titz, T. Jahnke, A. Czasch, M. S. Schöffler, K. Kreidi, O. Jagutzki, H. Schmidt-Böcking, and R. Dörner, *Phys. Rev. Lett.* **104**, 103201 (2010).
- [85] M. R. Jana, P. N. Ghosh, B. Bapat, R. K. Kushawaha, K. Saha, I. A. Prajapati, and C. P. Safvan, *Phys. Rev. A* **84**, 062715 (2011).
- [86] A. Khan, L. C. Tribedi, and D. Misra, *Phys. Rev. A* **92**, 030701(R) (2015).
- [87] M. Alagia, P. Candori, S. Falcinelli, M. Lavollée, F. Pirani, R. Richter, S. Stranges, and F. Vecchiocattivi, *J. Phys. Chem. A* **113**, 14755 (2009).

- [88] J. Eland, S. Plogmaker, P. Lablanquie, F. Penent, J. Palaudoux, C. Nicolas, E. Robert, C. Miron, and R. Feifel, *Chem. Phys. Lett.* **646**, 31 (2016).
- [89] J. H. Sanderson, T. R. J. Goodworth, A. El-Zein, W. A. Bryan, W. R. Newell, A. J. Langley, and P. F. Taday, *Phys. Rev. A* **65**, 043403 (2002).
- [90] W. A. Bryan, W. R. Newell, J. H. Sanderson, and A. J. Langley, *Phys. Rev. A* **74**, 053409 (2006).
- [91] C. Wu, C. Wu, D. Song, H. Su, Y. Yang, Z. Wu, X. Liu, H. Liu, M. Li, Y. Deng, Y. Liu, L.-Y. Peng, H. Jiang, and Q. Gong, *Phys. Rev. Lett.* **110**, 103601 (2013).
- [92] B. Wales, E. Bisson, R. Karimi, S. Beaulieu, A. Ramadhan, M. Giguère, Z. Long, W.-K. Liu, J.-C. Kieffer, F. Légaré, and J. Sanderson, *J. Electron Spectrosc. Relat. Phenom.* **195**, 332 (2014).
- [93] J. Rajput, T. Severt, B. Berry, B. Jochim, P. Feizollah, B. Kaderiya, M. Zohrabi, U. Ablikim, F. Ziaee, K. Raju P., D. Rolles, A. Rudenko, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Phys. Rev. Lett.* **120**, 103001 (2018).
- [94] T. Masuoka, I. Koyano, and N. Saito, *J. Chem. Phys.* **97**, 2392 (1992).
- [95] T. Masuoka, *J. Chem. Phys.* **98**, 6989 (1993).
- [96] R. Hall, L. Avaldi, G. Dawber, A. McConkey, M. MacDonald, and G. King, *Chem. Phys.* **187**, 125 (1994).
- [97] K. Saha, S. Banerjee, and B. Bapat, *Chem. Phys. Lett.* **607**, 85 (2014).
- [98] A. Ramadhan, B. Wales, R. Karimi, I. Gauthier, M. MacDonald, L. Zuin, and J. Sanderson, *J. Phys. B* **49**, 215602 (2016).
- [99] B. Wales, T. Motojima, J. Matsumoto, Z. Long, W.-K. Liu, H. Shiromaru, and J. Sanderson, *J. Phys. B* **45**, 045205 (2012).
- [100] H. Kumar, P. Bhatt, C. P. Safvan, and J. Rajput, *J. Chem. Phys.* **148**, 064302 (2018).
- [101] Z. Shen, E. Wang, M. Gong, X. Shan, and X. Chen, *J. Chem. Phys.* **145**, 234303 (2016).
- [102] A. M. Sayler, E. Wells, K. Carnes, and I. Ben-Itzhak, in *The CAARI 2000: Sixteenth International Conference on the Application of Accelerators in Research and Industry*, edited by I. L. Morgan, J. L. Duggan, and M. Hall, AIP Conf. Proc. No. 576 (AIP, Melville, NY, 2001), p. 33.
- [103] A. M. Sayler, J. Maseberg, D. Hathiramani, K. Carnes, and I. Ben-Itzhak, in *Application of Accelerators in Research and Industry: 17th International Conference on the Application of Accelerators in Research and Industry* edited by J. L. Duggan, I. L. Morgan, and M. Hall, AIP Conf. Proc. No. 680 (AIP, Melville, NY, 2003), p. 48.
- [104] P. Bunker, O. Bludsky, P. Jensen, S. Wesolowski, T. V. Huis, Y. Yamaguchi, and H. Schaefer, *J. Mol. Spectrosc.* **198**, 371 (1999).
- [105] K. Codling and L. J. Frasinski, *J. Phys. B* **26**, 783 (1993).
- [106] A. Rudenko, V. Makhija, A. Vajdi, T. Ergler, M. Schürholz, R. K. Kushawaha, J. Ullrich, R. Moshhammer, and V. Kumarappan, *Faraday Discuss.* **194**, 463 (2016).
- [107] T. Ando, A. Iwasaki, and K. Yamanouchi, *Phys. Rev. Lett.* **120**, 263002 (2018).
- [108] L. Holmegaard, J. L. Hansen, L. Kalhøj, S. L. Kragh, H. Stapelfeldt, F. Filsinger, J. Küpper, G. Meijer, D. Dimitrovski, M. Abu-samha, C. P. J. Martiny, and L. B. Madsen, *Nat. Phys.* **6**, 428 (2010).
- [109] J. L. Hansen, L. Holmegaard, J. H. Nielsen, H. Stapelfeldt, D. Dimitrovski, and L. B. Madsen, *J. Phys. B* **45**, 015101 (2011).
- [110] R. Johansen, K. G. Bay, L. Christensen, J. Thøgersen, D. Dimitrovski, L. B. Madsen, and H. Stapelfeldt, *J. Phys. B* **49**, 205601 (2016).
- [111] P. Sándor, A. Sissay, F. Mauger, P. M. Abanador, T. T. Gorman, T. D. Scarborough, M. B. Gaarde, K. Lopata, K. J. Schafer, and R. R. Jones, *Phys. Rev. A* **98**, 043425 (2018).
- [112] J. Eland, *Mol. Phys.* **61**, 725 (1987).
- [113] D. Pavičić, K. F. Lee, D. M. Rayner, P. B. Corkum, and D. M. Villeneuve, *Phys. Rev. Lett.* **98**, 243001 (2007).
- [114] M. Oppermann, S. J. Weber, L. J. Frasinski, M. Y. Ivanov, and J. P. Marangos, *Phys. Rev. A* **88**, 043432 (2013).
- [115] B. Jochim, R. Erdwien, Y. Malakar, T. Severt, B. Berry, P. Feizollah, J. Rajput, B. Kaderiya, W. L. Pearson, K. D. Carnes, A. Rudenko, and I. Ben-Itzhak, *New J. Phys.* **19**, 103006 (2017).
- [116] M. Hochlaf, F. R. Bennett, G. Chambaud, and P. Rosmus, *J. Phys. B* **31**, 2163 (1998).

4.3 H₂ roaming in alcohol molecules

Here, we present a publication in *Nature Communications* focusing on H₃⁺ formation from various alcohol molecules. The study was performed on two fronts, using time-resolved mass spectrometry measurements and quantum dynamics simulations conducted by our collaborators at Michigan State University and COLTRIMS measurements performed here in the J.R. Macdonald Laboratory at Kansas State University, which I led. Focusing on the COLTRIMS measurements, to compare the H₃⁺ formation rates between molecules, we calculated the branching ratios including all non-negligible channels resulting from the double ionization of each molecule. This way, we accounted for any differences in the target densities as well as corrected for the differences in the total double-ionization probability, at least to first order. With this analysis, we observed that the H₃⁺ branching ratio dropped significantly for longer carbon chains. Furthermore, molecular dynamics trajectory calculations suggested that H₂ roaming leading to H₃⁺ formation can occur following the double ionization. To our knowledge, this is among the first studies suggesting that roaming can occur in molecular ions.

In addition, we studied the CH₃CD₂OD and CD₃CH₂OH isotopologues of ethanol to elucidate some of the site-specific origins of the hydrogen atoms forming H₃⁺. Unsurprisingly, we found that all possible pathways contribute, though the strongest tend to involve the hydrogens emitted from the “middle” (i.e. α) carbon, which theory suggested are predominantly involved in the roaming process. Further discussion of these pathways is presented in this paper’s supplementary material, which we included in Appendix [B](#).

ARTICLE

DOI: 10.1038/s41467-018-07577-0

OPEN

H₂ roaming chemistry and the formation of H₃⁺ from organic molecules in strong laser fields

Nagitha Ekanayake¹, Travis Severt², Muath Nairat¹, Nicholas P. Weingartz¹, Benjamin M. Farris¹, Balram Kaderiya², Peyman Feizollah², Bethany Jochim², Farzaneh Ziaee², Kurtis Borne², Kanaka Raju P.², Kevin D. Carnes², Daniel Rolles², Artem Rudenko², Benjamin G. Levine¹, James E. Jackson¹, Itzik Ben-Itzhak² & Marcos Dantus^{1,3}

Roaming mechanisms, involving the brief generation of a neutral atom or molecule that stays in the vicinity before reacting with the remaining atoms of the precursor, are providing valuable insights into previously unexplained chemical reactions. Here, the mechanistic details and femtosecond time-resolved dynamics of H₃⁺ formation from a series of alcohols with varying primary carbon chain lengths are obtained through a combination of strong-field laser excitation studies and ab initio molecular dynamics calculations. For small alcohols, four distinct pathways involving hydrogen migration and H₂ roaming prior to H₃⁺ formation are uncovered. Despite the increased number of hydrogens and possible combinations leading to H₃⁺ formation, the yield decreases as the carbon chain length increases. The fundamental mechanistic findings presented here explore the formation of H₃⁺, the most important ion in interstellar chemistry, through H₂ roaming occurring in ionic species.

¹Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA. ²J. R. Macdonald Laboratory, Physics Department, Kansas State University, Manhattan, KS 66506, USA. ³Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824, USA. Correspondence and requests for materials should be addressed to M.D. (email: dantus@chemistry.msu.edu)

As one of the most abundant, yet simplest, triatomic cations in the universe, the trihydrogen cation^{1,2} (H_3^+) plays a vital role in interstellar gas-phase chemistry by facilitating the formation of molecules such as water and hydrocarbons. Clues regarding the fundamental dynamics and mechanisms of these chemical processes may be obtained from laser-induced dissociation processes producing H_3^+ . The production of H_3^+ from various organic molecules following excitation with intense femtosecond laser pulses has been reported previously^{3–13}. However, the exact mechanism(s), timescale(s), and yield(s) for this reaction have remained a mystery. In a recent study¹⁴, we provided experimental and theoretical evidence for the existence of two reaction pathways for the formation of H_3^+ from methanol under strong-field ionization. In brief, both reaction pathways are initiated by the ultrafast double ionization of the parent molecule and proceed through prompt formation of a roaming neutral H_2 moiety from the methyl site. By roaming, here we imply that a neutral fragment explores relatively flat regions of the potential energy surface far from the minimum energy path^{15–19}. In doubly ionized methanol, the roaming H_2 fragment abstracts a third proton from the methyl carbon or from the hydroxyl oxygen leading to the formation of H_3^+ . Experimental findings for methanol and its isotopologues showed that the proton transfer is faster from carbon than from oxygen. In both these H_3^+ formation pathways, the multiple bond cleavage and bond formation processes, and the roaming of the neutral H_2 moiety, all occur within a 100–250 fs timescale in our experiments. This recent finding, associating neutral H_2 roaming with the formation of H_3^+ under strong-field excitation, inspired a series of additional experiments aimed at elucidating aspects of this novel chemical reaction mechanism.

The recent recognition of roaming mechanisms has deepened our understanding of certain exotic chemical reactions^{15–19}. Roaming has been widely observed in highly excited polyatomic molecules, for which photodissociation proceeds through trajectories other than the minimum energy pathway. Typically, roaming takes place on a flat region of the potential energy surface, thus allowing nascent reaction products to remain near each other long enough for further reactions to occur. Of particular interest to the work presented, recent studies have focused on roaming processes in small organic molecules such as acetaldehyde^{20–22}, acetone²³, methyl formate^{24–26}, and propane²⁷. In most cases, the roaming pathway contributes a small fraction of the total yield. However, certain photodissociation pathways, such as the visible light-induced $\text{NO}_3 \rightarrow \text{NO} + \text{O}_2$ decomposition reaction, occur solely via a roaming mechanism^{28,29}. Similarly, the roaming of a neutral hydrogen molecule is essential for H_3^+ formation from the methanol dication¹⁴.

While roaming mechanisms have been well established in neutral molecules, the same cannot be said about ionic species. Outside of our work, to the best of our knowledge there is only one theoretical prediction of H_2 roaming in the dissociative ionization of allene³⁰. A theoretical analysis on the H_3^+ formation reaction from ethane identified a transition state with a H_2 molecule attached to a $\text{C}_2\text{H}_4^{2+}$ ion⁸. However, in that study, no evidence was provided confirming H_2 roaming during the dissociation of the ethane dication. Based on the above background, together with our previous work¹⁴, one might speculate that all H_3^+ formation pathways originating from organic molecules require neutral H_2 roaming, regardless of whether such mechanisms are initiated by charged particles or intense femtosecond laser fields. While scientifically confirming or refuting the validity of such a general statement is beyond the scope of this work, a systematic study of H_3^+ formation reactions on a family of molecules can provide valuable information about this relatively unknown H_2 roaming mechanism in ionic species. Our

work on the simplest alcohol cation¹⁴, and the follow-up experimental and theoretical work presented here on a series of alcohols, constitute most of what is known about H_2 roaming and H-migration mechanisms occurring in ionic species. Here the roaming H_2 molecule acts as a Brønsted–Lowry base,^{31,32} accepting a proton from the highly acidic doubly-charged fragment ion.

As the initiator of many interstellar chemical reactions, H_3^+ is a catalyst for the formation of dense molecular clouds containing complex organic molecules^{33,34}. The formation reaction³⁵, existence in interstellar space^{36,37}, and spectroscopic properties³⁸ of the H_3^+ ion, as well as its importance in the ion chemistry of interstellar molecular clouds are well documented^{39–41}. In interstellar media, an environment rich in molecular hydrogen, protonation of molecular hydrogen is initiated by cosmic radiation. As proposed by Hogness and Lunn³⁵, a bimolecular reaction involving neutral and singly ionized hydrogen molecules yields H_3^+ , i.e., $\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$. It is worth noting here that the proton abstraction by H_2 observed in methanol resembles the Hogness and Lunn reaction leading to the formation of H_3^+ . In addition to its formation through femtosecond laser excitation, H_3^+ has been observed from certain organic molecules via electron impact^{42–44}, proton impact^{45–47}, and highly-charged ion collision^{48,49} under laboratory conditions. Most of what is known about H_3^+ chemistry comes from reactive scattering experiments and from ion-neutral reactions in flow drift tubes. These measurements, full collisions, provide reaction cross sections and in some cases angle-resolved product state distributions^{50–52}. Unimolecular photodissociation reactions, half collisions^{53,54}, proceed from a well-defined geometry and can be studied with femtosecond time resolution⁵⁵. Here we apply the concept of half-collision to learn about the femtosecond dynamics of reactions involving H_3^+ produced from alcohols⁵⁶ and their importance in astrochemistry in the formation of larger complex molecules through protonation^{57,58}. Our study helps reveal dynamics and mechanistic details that are not measurable in reactive ion-neutral scattering studies. Furthermore, our findings are relevant to chemistry initiated by cosmic radiation including photons and electrons with energies in the 30–100 eV range. Given the abundance of hydrogen in organic compounds, solvents, and fuels, the neutral hydrogen roaming chemical reactions discussed in this work may be relevant to condensed-phase chemical reactions involving superacids⁵⁹, soot formation in combustion chemistry⁶⁰, charged particle-impact-induced chemical reactions⁶¹, and gas-phase acid/base reactions including those that formed the first organic compounds in the universe².

In this article, we examine the involvement of H_2 roaming mechanisms in ionic species in the formation of H_3^+ from a series of alcohols under strong-field excitation and investigate the effect that longer carbon chains have on the yield of H_3^+ . The formation pathways of H_3^+ via the roaming H_2 mechanism for methanol and ethanol, which are triggered by the strong-field double ionization of the corresponding parent molecule, are shown in Fig. 1. When comparing the doubly-charged structures to their neutral counterparts, one can clearly see the elongation of C–H bonds and the narrowing of the H–C–H angle on the α -carbon atom. Based on our previous study¹⁴, we consider that these intramolecular changes are the primary motions leading to the formation of neutral H_2 and eventually of H_3^+ . Here we evaluate the validity of this mechanism and the influence of alkyl-chain length by extending our work to a series of primary alcohol molecules: methanol (CH_3OH), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), and 1-propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$). Findings for a secondary alcohol, 2-propanol ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$), and a tertiary alcohol, *tert*-butanol ($(\text{CH}_3)_3\text{COH}$), species that cannot react as proposed in Fig. 1, are then compared. Through in-depth experimental analysis of

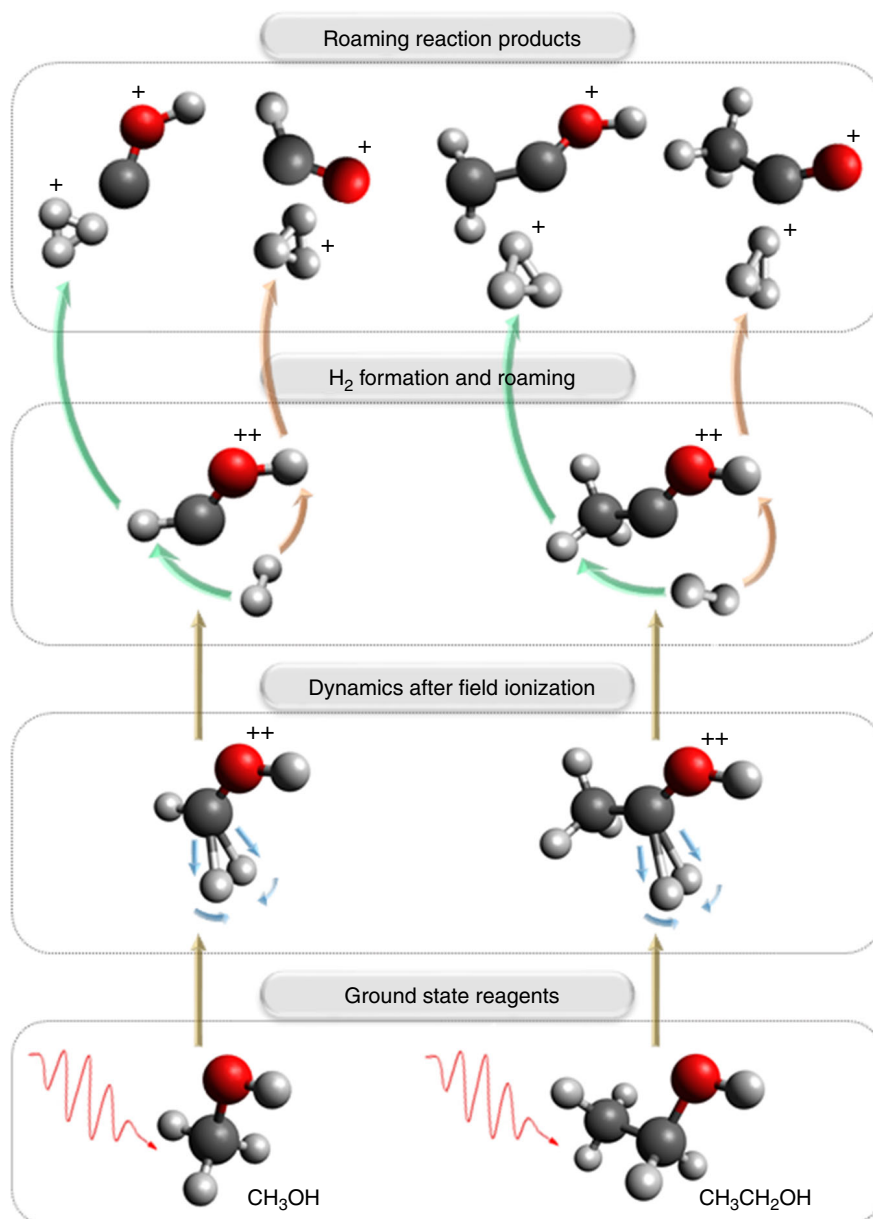


Fig. 1 Primary H_3^+ formation pathways from methanol (CH_3OH) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$). Formation occurs via the neutral H_2 roaming mechanism under strong-field laser ionization. In both molecules, the carbon atom attached to the hydroxyl functional group is referred to as the α -carbon and the corresponding hydrogen atoms are referred to as α -hydrogens. In the case of ethanol, the terminal carbon atom and hydrogen atoms are referred to as the β -carbon and the β -hydrogen atoms, respectively

product yields and timescales of formation at a peak laser intensity of $2.0 \times 10^{14} \text{ W cm}^{-2}$, we show that H_3^+ yield decreases as the primary carbon chain length increases. Furthermore, we reveal additional formation mechanisms available for the production of H_3^+ in small alcohols, particularly from ethanol.

Results

Experimental H_3^+ yields. In order to compare H_3^+ production from different alcohols upon ultrafast double ionization, we employed two distinct experimental setups and analysis methods. Using time-of-flight (TOF) mass spectrometry, we are able to compare the total yield of H_3^+ (i.e. the integral over that peak) for each of the different alcohols. Complete TOF mass spectra (TOF-MS) for methanol, ethanol, 1-propanol, 2-propanol, and *tert*-butanol are given as Supplementary Information Figs. 1–5. For

these measurements we carefully controlled the laser excitation and the target density. In order to quantify the H_3^+ branching ratio following double ionization, we carried out coincidence TOF (CTOF) measurements where we directly counted the number of events leading to the H_3^+ formation relative to all dications produced. Further information regarding experimental techniques, setups, and parameter settings can be found in the Methods section.

Quantifying the CTOF branching ratio requires consideration of every coincidence ion pair associated with the production of H_3^+ . Specifically, we determined the sum of all measured ion pairs containing H_3^+ (i.e. $\text{H}_3^+ + m_X^+$) divided by the sum of all single ions and ion pairs originating from the parent dication (i.e. all dication products). Extraction of the pair coincidences is illustrated in Supplementary Fig. 6. The analytical expression for

the CTOF branching ratio is given in the Methods: Experimental setup section (Eq. 2). As explained in Supplementary Note 1, this method has the advantage that it allows a direct comparison of branching ratios among different molecules. While this accounting is relatively easy to do for methanol, it is challenging for ethanol, and very complicated and time consuming for larger molecules. The results from our measurements on a series of alcohols are presented in Fig. 2. The first column (purple) corresponds to the CTOF-determined branching ratio, the second column (light green) corresponds to the integrated H_3^+ TOF yield ($[\text{H}_3^+]$), and the third column (dark green) corresponds to the H_3^+ TOF yield normalized by the total number of ions detected. For comparison, the TOF measurements have been normalized to the measured H_3^+ branching ratio of methanol obtained by CTOF measurements.

What is immediately visible in Fig. 2 is the reduction in the H_3^+ formation with increasing carbon chain length, regardless of the measurement technique or the normalization method. Formation of H_3^+ is most prominent from methanol, even though it has fewer hydrogen atoms per molecule than the other molecules of interest. In the case of ethanol, the production of H_3^+ is smaller by a factor of about 5 or 3 (for the CTOF and TOF data, respectively) compared to that of methanol. This observation seems counterintuitive; ethanol contains 50% more hydrogen atoms than methanol, suggesting that additional H_3^+ formation pathways might have been expected, resulting in a higher H_3^+ yield. To our surprise, upon further lengthening the carbon chain, i.e. in the case of 1-propanol, the total H_3^+ production drops by an additional factor of 11 or 2 (for CTOF and TOF measurements, respectively) compared to ethanol.

When expressed as a fractional yield, i.e. $[\text{H}_3^+]/[\text{all ions}]$ (dark green column in Fig. 2), the TOF results follow a similar trend as observed with total H_3^+ branching ratios for the smaller three molecules for which CTOF measurements are not too demanding. Though the fractional yield is proportional to the branching ratio for H_3^+ production, a derivation detailed in the Supplementary Note 1 indicates that the proportionality coefficient depends on the ratio of single to double ionization probabilities, denoted by σ_1 and σ_2 , respectively. Explicitly this relation is given

by

$$\sum_j F_2(3, j) \simeq \left(\frac{\sigma_1}{\sigma_2} + 1 \right) \frac{M(3)}{\sum_k M(k)}, \quad (1)$$

where $F_2(3, j)$ is the branching ratio of $\text{H}_3^+ + m_j^+$ and $M(i)$ is the number of counts measured in a specific TOF peak associated with mass m_j (assuming singly-charged for simplicity). In spite of the additional dependence on the ionization probabilities, the trend evaluated using the fractional H_3^+ yield is in reasonable agreement with the branching ratios evaluated directly from the CTOF measurements. This suggests that the σ_1 to σ_2 ratio, which can vary significantly from one molecule to another, varies slowly for the group of molecules in our study. The most likely explanation is that double ionization occurs predominantly from the oxygen atom in the hydroxyl group that is common in all these molecules.

Through our analysis, we learn that the TOF fractional H_3^+ production allows the discovery of H_3^+ formation trends, and that even a direct comparison of the measured TOF H_3^+ yield is consistent with the more complex and in-depth analysis-dependent CTOF method as long as one can maintain the experimental conditions between measurements on different molecules under tight control and the single to double ionization probability does not change significantly between molecules. It is worth noting here that the discrepancy in the CTOF and TOF data for 1-propanol could be attributed to the production of some H_3^+ from the mono-cation of 1-propanol (a more detailed error analysis is provided in Supplementary Note 2 and Supplementary Figs. 7–9). Having established the qualitative trends of both methods, and calibrated the TOF data with the best numbers obtained by CTOF on methanol, we are able to evaluate trends among the larger alcohols.

In Fig. 2, we observe that the integrated H_3^+ yield as well as the fractional H_3^+ yield from 1-propanol and 2-propanol, which have the same number of hydrogen atoms (and, most likely, have similar photoionization rates), is comparable within the measurement error. Clearly, the arrangement of hydrogen atoms within the molecules is significantly different; however, 2-propanol

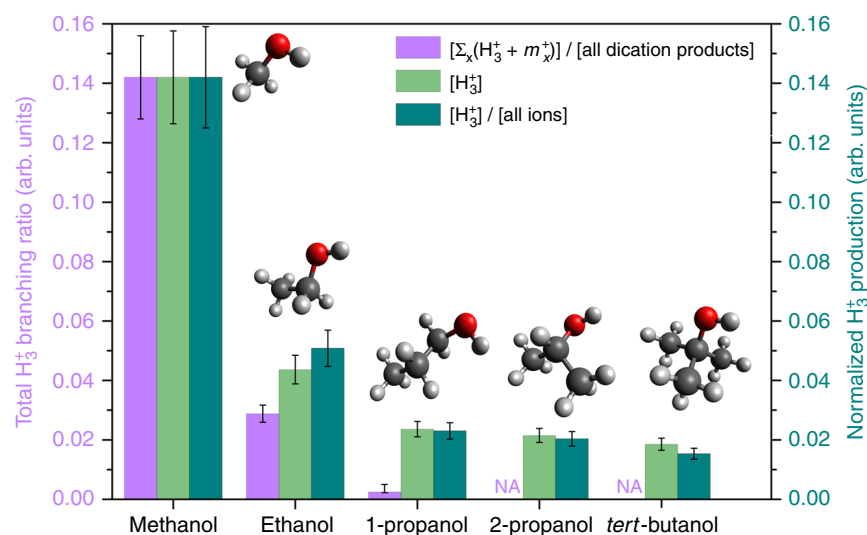


Fig. 2 H_3^+ production from a series of alcohols. Total H_3^+ branching ratios ($[\Sigma_x(\text{H}_3^+ + m_x^+)]/[\text{all dication products}]$) together with normalized H_3^+ ($[\text{H}_3^+]$), and fractional H_3^+ ($[\text{H}_3^+]/[\text{all ions}]$) production from dissociative ionization of methanol, ethanol, 1-propanol, and 2-propanol together with *tert*-butanol in a linearly polarized laser field with a peak intensity of $2.0 \times 10^{14} \text{ W cm}^{-2}$. The $[\text{H}_3^+]$ and $[\text{H}_3^+]/[\text{all ions}]$ yields were obtained through the TOF technique, and each of them is normalized with respect to the corresponding branching ratio of methanol, $[(\text{H}_3^+ + \text{HCO}^+)]/[\text{all dication products}]$, determined by the CTOF method. Due to the complexity of quantitative analysis (see text for details), CTOF measurements were not performed for large molecules (2-propanol and *tert*-butanol) and indicated by “NA” at the corresponding positions in the figure. Data are provided as Supplementary Table 1

possesses a single α -hydrogen atom, which plays a key role in H_3^+ formation as we discuss in a later section of this work. In the case of *tert*-butanol, which has three terminal methyl groups and no α -hydrogen atom in its structure, we expected a reduction in the H_3^+ yield. However, no such reduction is observed. The observation of H_3^+ formation from *tert*-butanol implies that an H_3^+ formation mechanism exists that primarily involves hydrogen atoms from terminal methyl groups, without an involvement of α -hydrogen atoms. This observation is in agreement with the formation of H_3^+ from acetone¹⁴, in which hydrogen migration is not favorable and H_3^+ is solely produced from terminal methyl groups.

Electronic structure calculations. Ab initio electronic structure calculations play an important role in further explaining the observed yields and branching ratios. Further information regarding electronic structure calculations is provided in the Methods: Ab initio calculations and simulations section and in Supplementary Note 3. In methanol, upon instantaneous double ionization of the parent molecule, the positive charges that build up on the oxygen atom draw electron density from the methyl group, thus decreasing the electron density on the hydrogen atoms, as shown in the calculated Mulliken population analysis for the neutral and doubly-charged molecules (Supplementary Fig. 11). This results in weakening of the C–H bonds, causing elongation and favoring detachment of H_2 from the parent C atom (Supplementary Fig. 10), an essential step in initiating the roaming mechanism leading towards the formation of H_3^+ . In the case of ethanol, the depletion of electron density on the α -carbon and the α -hydrogen atoms is partially compensated by the terminal methyl group. Therefore, the α -hydrogen atoms are less positively charged in the ethanol dication than in the methanol dication, as evident in the Mulliken population analysis of doubly-charged ethanol (Supplementary Fig. 11). One can also see that the positive charge on the β -carbon hydrogen atoms is smaller than the α -carbon ones; we therefore surmise that the β -carbon C–H bonds are less likely to favor H_2 detachment, resulting in a reduced yield of H_3^+ . The further reduction in H_3^+ yield found for 1-propanol can be attributed to the fact that the electronic induction from the terminal ethyl group is higher than that of the methyl group (Supplementary Fig. 11).

New H_3^+ formation pathways. While Fig. 1 shows the primary mechanism for H_3^+ formation, the trends observed in Fig. 2 for the different alcohols indicate that other formation pathways exist. Here we address the different mechanisms for H_3^+ formation available to alcohols, focusing initially on the two-body fragmentation of ethanol. The complexity arising from having a larger number of hydrogen atoms is addressed by the judicious selection of partially deuterated ethanol isotopologues, which allows us to identify and clearly distinguish several different H_3^+ formation pathways.

Figure 3 presents CTOF spectra from dissociative ionization of (a) CH_3CD_2OD and (b) CD_3CH_2OH obtained at a peak laser intensity of $3.0 \times 10^{14} \text{ W cm}^{-2}$, in which four H_3^+ formation pathways were clearly identified. Each correlated pair of ions (two-body breakup channel) occurs as a narrow diagonal streak on the two-dimensional ion arrival time map as a result of momentum conservation, for example the ion pair D_3^+ and $C_2H_3O^+$. Data from an ion pair, with the second fragment having a lower mass (lower in the column) is associated with three-body dissociation involving neutral H or H_2 , and because the neutral fragment carries some momentum, the diagonal streak is broadened. Data from an ion pair, with the second fragment having a higher mass (higher in the column), is associated with a

^{13}C isotopic impurity in the sample (further details pertaining to interpreting the CTOF spectra can be found in Supplementary Information Note 4 and Supplementary Fig. 12). For simplicity, we focus our discussion only on two-body breakup channels leading to the formation of H_3^+ , which are labeled on Fig. 3. In Fig. 3a, we observe a well-defined, strong coincidence channel that corresponds to the formation of D_3^+ . As supported by ab initio simulations (described later), we consider that D_3^+ formation proceeds via dissociation of a neutral D_2 moiety from two deuterium atoms bound to the α -carbon followed by roaming and abstraction of the third proton from the hydroxyl group. This pathway is quite similar to what we observed in methanol¹⁴, in which the neutral H_2 formed from the methyl group abstracts the hydroxyl proton to form H_3^+ . The next prominent channel in Fig. 3a corresponds to the formation of HD_2^+ , likely resulting when a similar neutral D_2 moiety abstracts a β -hydrogen atom from the terminal methyl group. However, in our ab initio simulations, we observe that a roaming H_2 moiety can be formed from one α - and one β -hydrogen. Therefore, in the formation of HD_2^+ , we cannot exclude the possibility of an α -deuterium and a β -hydrogen migrating (as an HD fragment) and abstracting the oxygen-bound deuterium. Unfortunately, due to m/z degeneracy, the remaining two channels shown in Fig. 3a, i.e. H_2D^+ (with D_2^+) and H_3^+ (with HD^+), do not provide conclusive evidence for any further pathways. However, as shown in Fig. 3b, by using CD_3CH_2OH we can isolate two additional channels for H_3^+ formation from ethanol, primarily involving β -deuterium atoms. The HD_2^+ formation channel results from two β -deuterium atoms associating with a single α -hydrogen atom or the oxygen-bound hydrogen. The fourth pathway we identified from CD_3CH_2OH is D_3^+ formation, which only involves β -deuterium atoms from the terminal methyl group. As evident in the later described ab initio simulations, these latter two pathways are most likely initiated by the migration of an α -hydrogen to the terminal methyl site, which enables the ejection of β -hydrogens. Beyond the identification of the above four pathways, further analysis regarding the multiple H_3^+ formation mechanisms will be presented elsewhere, in order to maintain the focus of this Communication on comparisons found among different alcohol molecules.

Returning to Fig. 2, it is noteworthy that 1-propanol, 2-propanol, and *tert*-butanol have approximately the same H_3^+ yield, within experimental errors. For 1-propanol, one might expect H_3^+ formation paths similar to those described for ethanol, namely the primary pathway described in Fig. 1, and H-migration. However, for 2-propanol the primary mechanism as described in Fig. 1 is no longer available. Therefore, H_3^+ formation must follow migration of the α -hydrogen toward either of the methyl groups, or occur directly from hydrogens of the methyl groups. Perhaps having two terminal methyl groups instead of one compensates for the absence of two α -carbon bound hydrogen atoms. Direct formation of H_3^+ from a terminal methyl group seems to be the most probable mechanism available for *tert*-butanol, but having three such terminal methyl groups makes up for not having an H-migration pathway available.

H_3^+ formation timescales. The formation timescale of H_3^+ was experimentally obtained using a femtosecond pump-probe technique, which utilizes a strong pump pulse to generate the reaction precursor, the doubly-charged parent ion, and a weak probe pulse to interrupt the formation of H_3^+ . Figure 4 presents the H_3^+ yield from methanol as a function of pump-probe time delay over a time period of 1.0 ps. A detailed description of time-dependent features of the complete transient (see Fig. 4 inset) can be found in our previous work¹⁴. In brief, a strong pump pulse creates the

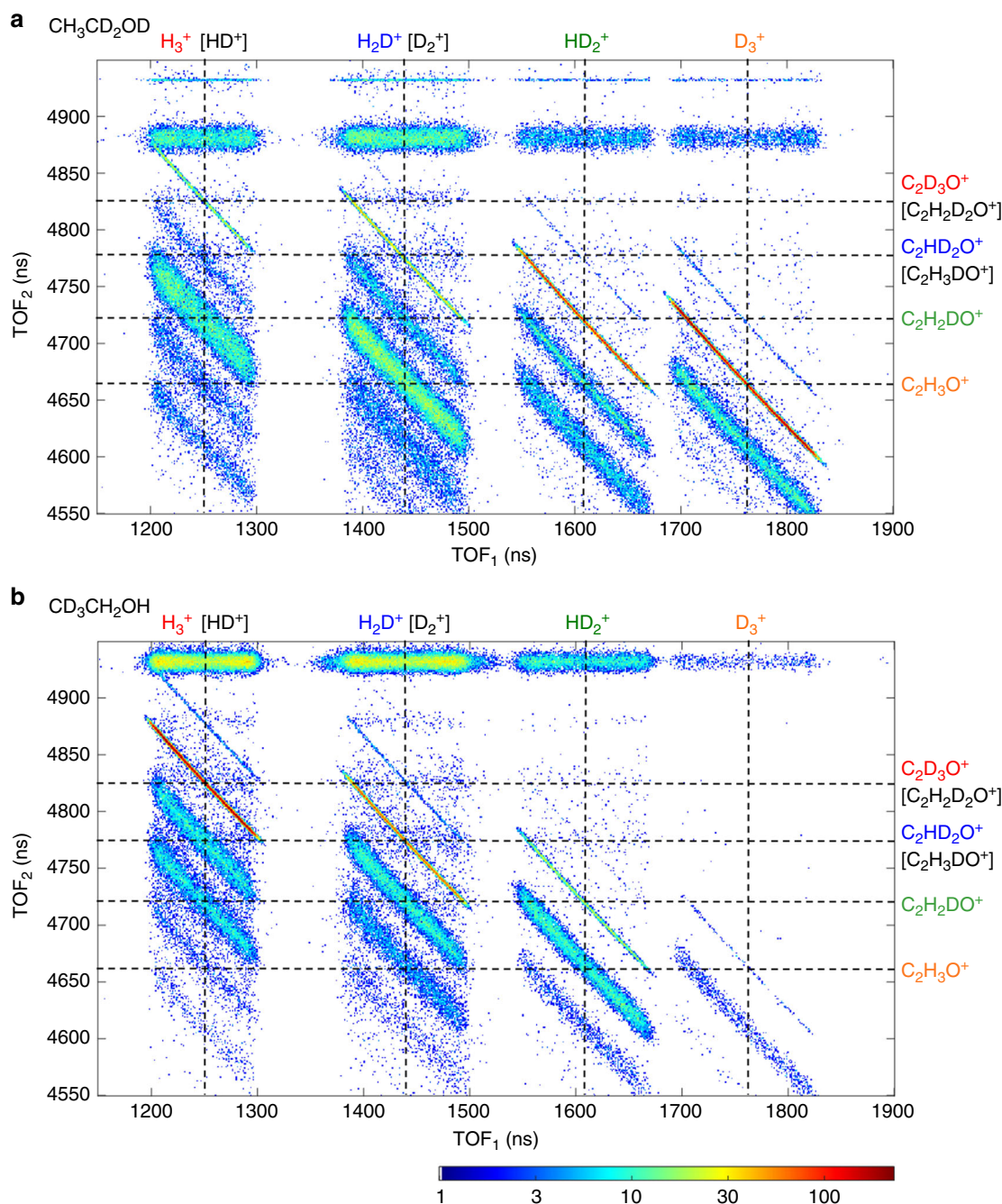


Fig. 3 H_3^+ formation from ethanol. Truncated coincidence time-of-flight maps focused only on H_3^+ production in two-body channels from dissociative ionization of **a** $\text{CH}_3\text{CD}_2\text{OD}$ and **b** $\text{CD}_3\text{CH}_2\text{OH}$ in a linearly polarized laser pulse centered about 790 nm, 23-fs long with a peak intensity of $3.0 \times 10^{14} \text{ W cm}^{-2}$. The labeled dashed lines indicate the two-body breakup ion pairs related to H_3^+ formation from the ethanol dication. The logarithmic color scale depicts the number of ion pairs recorded

parent dication, which is then fragmented by the time-delayed weak probe pulse, thus preventing the formation of H_3^+ . For short delay times, the probe arrives prior to the formation of H_3^+ , the parent dication fragments and we observe a depletion in the H_3^+ yield. The incremental time delay between pump and probe pulses results in an exponential rise that tracks the H_3^+ formation time and reaches a plateau at long time delays > 500 fs. Using a mono-exponential fit given by $y = y_0 + A(1 - \exp(-t/\tau))$, where A is the amplitude, y_0 is the offset, and τ is the time constant, we extracted the formation time of H_3^+ . Considering a 95% confidence level for the fit parameters, we observed a fast formation of H_3^+ from methanol, specifically $\tau = 102 \pm 7$ fs, which is in good agreement with our previous work¹⁴ ($\tau = 98 \pm 4$ fs).

Furthermore, as observed in previously published *ab initio* molecular dynamics simulations¹⁴, the measured value is in good agreement with the H_3^+ formation time range of 50–150 fs for the mechanism involving the three hydrogen atoms from the methyl group.

Figure 5 presents the pump-probe transients of H_3^+ yields as a function of applied time delay over a time period of 1.0 ps for ethanol, 1-propanol, and 2-propanol. Subsequent to a similar exponential fit described previously, ethanol and 1-propanol exhibit formation times a factor of 2.3 ± 0.2 longer than for methanol, while the formation time for H_3^+ from 2-propanol only increased by a factor of 1.9. Our previous study¹⁴ found that the roaming H_2 molecule abstracts the third proton from the

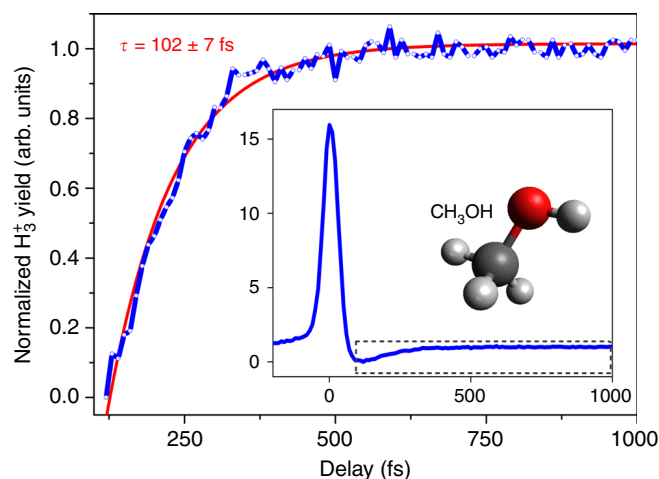


Fig. 4 Pump-probe transient for H_3^+ production from methanol (CH_3OH). Normalized H_3^+ yield (blue solid line) together with an exponential fit (red solid line) from dissociative ionization of methanol as a function of applied time delay between the pump and probe pulses. In the inset, the complete view of the normalized transient is shown where the dashed rectangle highlights the area of interest displayed in the main Figure. Normalization was performed such that the minimum value of the yield is 0 and the yield at large positive time delays (≥ 500 fs) is 1

same atom (carbon) faster (~ 100 fs) than from the adjacent atom (oxygen), due to the longer roaming time (and distance) of the neutral H_2 moiety. With no third α -hydrogen atom available in ethanol or 1-propanol, this latter, slower H_3^+ formation channel is expected to dominate, as supported by our ab initio simulations. Here the roaming H_2 molecule forms from the α -hydrogens and then abstracts the third hydrogen from the adjacent hydroxyl group. In both molecules, the H_3^+ formation from the terminal CH_3 group is assumed to be negligible (as justified by the very weak $\text{D}_3^+ + \text{CH}_2\text{OH}^+$ two-body coincidence channel in Fig. 3b). Interestingly, 2-propanol exhibits a formation time for H_3^+ slower than the dominant path in methanol, but faster than those of ethanol and 1-propanol. Clearly, a distinct formation mechanism takes over when the terminal methyl hydrogens must be involved.

Ab initio molecular dynamics simulations. An adequate first-principles molecular dynamics scheme for the fragmentation of ethanol requires a method that provides a balanced description across all potential closed and open shell fragments, such as the complete active space self-consistent field (CASSCF) method, which was implemented using an active space of 12 electrons in 12 orbitals. A summary of the final hydrogen dissociation products following ab initio molecular dynamics simulations of the photodissociation of doubly-ionized ethanol is reported in Table 1. We notice that the largest pathway is H^+ formation, which is in agreement with the experimental yield as the H^+ ion peak is the strongest. The H_2 and H_2^+ channels were minimal compared to H^+ . H_3^+ formation was not observed in our CASSCF trajectories due to the limited sampling afforded by these high-level calculations and the low H_2 formation yield.

Our main interest throughout the calculations is to understand and elucidate the H_3^+ formation mechanism in ethanol and whether it proceeds through formation of a roaming neutral H_2 followed by abstraction of a proton to form H_3^+ as found in methanol¹⁴. In hopes of observing H_3^+ formation, we have also carried out molecular dynamics simulations with the electronic structure computed at the quadratic configuration interaction singles and doubles (QCISD) level, which can adequately describe

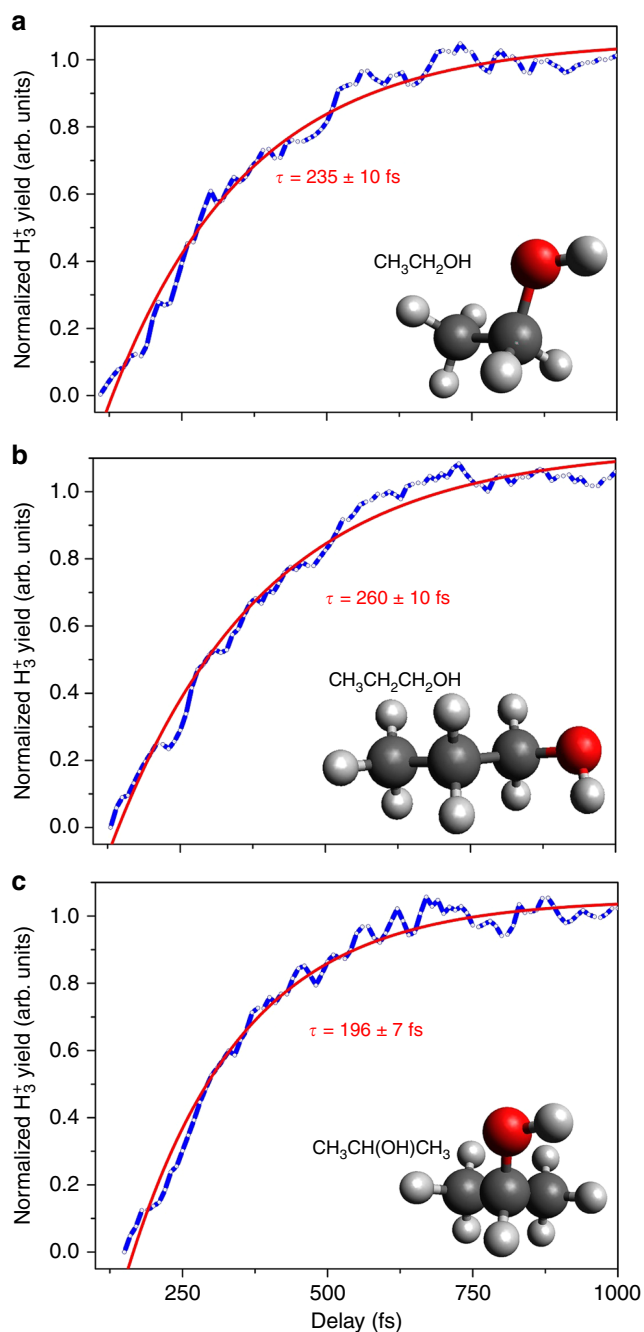


Fig. 5 Pump-probe transient for H_3^+ production from alcohols. Normalized H_3^+ transients from dissociative ionization of different alcohols as a function of applied pump-probe delay. Shown in the figure (in blue solid lines) are **a** H_3^+ from ethanol, **b** H_3^+ from 1-propanol, and **c** H_3^+ from 2-propanol. Normalization was performed as described in Fig. 4 caption. Corresponding exponential fits are shown by red solid lines

Table 1 Percentage of hydrogen species (summed over all channels) ejected from doubly-charged ethanol that are observed using CASSCF and QCISD ab initio molecular dynamics simulations

	CASSCF % yield	QCISD % yield
H^+ formation	38.6	30.1
H_2^+ formation	0.5	0
H_2 formation	2.6	57.9
H_3^+ formation	0	0.2

closed shell pathways, such as H_2 and H_3^+ formation. Though this method surely overestimates the probability of neutral H_2 formation, it also likely provides a very accurate representation of the dynamics following the formation of neutral H_2 . To support this assessment, we have benchmarked the validity of QCISD for the formation of H_3^+ relative to our previous CASSCF calculations¹⁴ using methanol as shown in the Supplementary Note 5. In the benchmark study, we noticed that QCISD was incapable of predicting the formation of the open shell fragment H_2^+ , and at the same time QCISD was biased toward H_2 and H_3^+ formation as can be deduced from their higher yields compared to the CASSCF results. The observed probability of H_3^+ formation upon release of H_2 was comparable at the CASSCF and QCISD levels, and the qualitative mechanism was observed to be similar regardless of method (Supplementary Table 2). This mechanism commences with the formation of a neutral H_2 moiety from the α -hydrogen atoms that roams for a brief period until it abstracts a proton from the terminal methyl site or the hydroxyl site. Thus, QCISD is sufficient to understand the H_2 formation pathways as well as H_3^+ production. Ethanol QCISD results are summarized in Table 1, which shows that H_2 formation is relatively high through which H_3^+ formation is observed as well.

Two videos of representative H_3^+ -forming molecular dynamics trajectories are included in the online Supplementary Information (Supplementary Videos 1 and 2). These videos show that H_2 forms from the two α -hydrogens, then roams and abstracts a proton from the hydroxyl group to form H_3^+ (snapshots of a trajectory are shown in Fig. 6). In our molecular dynamics simulations, all the observed H_3^+ trajectories (4 events out of 2000 trajectories) followed the same mechanism, in which a neutral roaming H_2 formed from two α -hydrogens, then abstracts the hydroxyl hydrogen on timescales between 110 and 220 fs. This is in good agreement with our experimental observations for ethanol presented in a previous section of this study.

The molecular dynamics trajectories were sampled from the ground state minima, which correspond to geometries far from minima on the doubly-charged potential energy surface. The excess energy results in vibrational excitation of multiple bonds and the possibility for multiple bond breaking. Here we focus on bond breaking that results in the formation of a roaming H_2 , which is the first step toward the production of H_3^+ . When tracing H_2 formation in ethanol we noticed three different pathways; the main pathway is from the two α -hydrogens, which accounts for about 65% from all the observed H_2 trajectories. The second pathway is initiated with the migration of an α -hydrogen to the β -carbon, followed by the formation of H_2 from one α - and one β -hydrogen. This second pathway was observed in about 29% of the H_2 trajectories. The remaining 6% of H_2 molecules were formed from two β -hydrogens. Interestingly, this pathway was initiated with the migration of an α -hydrogen to the β -carbon prior to the ejection of neutral H_2 , i.e. α -hydrogen migration preceded the ejection of two β -hydrogens. Videos showing these

three H_2 formation pathways are provided as Supplementary Videos 3–5.

Discussion

In summary, we have studied the reaction pathways and ultrafast dynamics associated with the formation of H_3^+ from a series of alcohol molecules with varying primary carbon chain lengths and molecular structures. Ab initio electronic structure calculations and molecular dynamics simulations, together with in-depth experimental data analysis allow us to refine our understanding of the relatively unknown mechanisms that lead to hydrogen molecule formation, roaming, and H_3^+ formation. The results presented in this Communication confirm the prevalence of roaming H_2 molecule mechanisms in the formation of H_3^+ . From our findings from methanol, ethanol, and 1-propanol, it is evident that the elongation of C–H bonds and narrowing of the H–C–H angle are the primary initial steps in the formation of neutral roaming H_2 . Our key experimental finding, supported by ab initio calculations, indicates that the yield of H_3^+ decreases as the carbon chain length increases from methanol to 1-propanol. The clear implication is that a mere increase in the number of hydrogen atoms does not necessarily result in increased H_3^+ yield as H_3^+ formation pathways are defined by unique features of the molecular structure, such as the prevalence of α -hydrogen atoms. Furthermore, through experimental evaluation of isotopically substituted ethanol, $\text{CH}_3\text{CD}_2\text{OD}$ and $\text{CD}_3\text{CH}_2\text{OH}$, we unraveled four distinct H_3^+ formation pathways for alcohol molecules with long primary carbon chain lengths. Observation of D_3^+ from ethanol isotopologue $\text{CD}_3\text{CH}_2\text{OH}$, and formation of H_3^+ from *tert*-butanol, together with our previous results from acetone¹⁴ point to the existence of a lower-yield pathway exclusively involving hydrogen atoms in a terminal methyl group.

The neutral H_2 roaming chemical reactions studied here provide insights into the exotic and hitherto unknown chemical processes occurring in our universe. Specifically, the combined experimental and theoretical work presented here explores the existence of roaming reactions occurring in ionic species, which have not been widely studied thus far. Based on time-resolved measurements following ultrafast double ionization of small alcohols and confirmed by molecular dynamics simulations, we observe that these H_2 roaming chemical reactions occur in the 100–260 fs timescale. Given that roaming fragments spend time in relatively flat regions of the potential energy surface, the dynamics of these reactions are much slower than those of direct unimolecular dissociation. These reactions take place following double ionization (27.0–30.5 eV) and involve hydrogen atoms, which are very light. Direct dissociation should be expected to be faster than 20 fs, especially because of the Coulombic repulsion within the small molecule. The measured reaction times (100–260 fs) are an order of magnitude slower than what one would expect if the reaction pathways did not involve roaming.

Details learned by studying the unimolecular photodissociation reactions, or “half collisions”^{53,54}, presented in this study enhance our understanding of H_3^+ reaction mechanisms (i.e. reactive

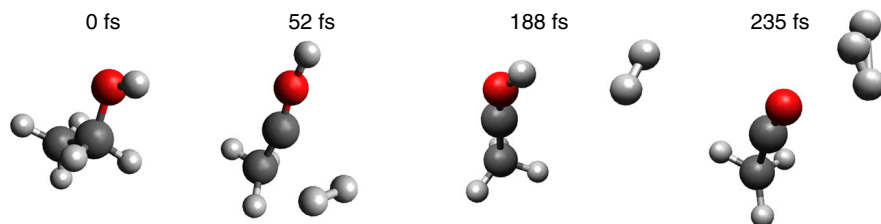


Fig. 6 Molecular dynamics trajectory for H_3^+ formation. Snapshots at different times from a representative trajectory showing formation of H_3^+ from ethanol calculated using QCISD ab initio molecular dynamics. The complete trajectory is provided as Supplementary Video 1

collisions). Most importantly, we find the H_2 roaming molecule behaves as a Brønsted–Lowry base, abstracting a proton to form H_3^+ . In turn, H_3^+ can behave as a Brønsted–Lowry acid, donating a proton in interstellar reactive collisions. These fundamental findings reveal an important aspect about molecular hydrogen formation from organic compounds under high-energy conditions, the chemistry mediated by the roaming hydrogen molecules, and improve our understanding of the chemical reactions that resulted in the organic compounds that likely led to life in the universe.

Methods

Experimental setup. A detailed description of experimental setups, parameter settings, and intensity calibration methods utilized in acquiring TOF-MS, pump-probe transients, and CTOF measurements can be found in our previous work¹⁴. Some salient information relevant to reproducing the data presented in this study are briefly stated below.

Both TOF-MS and pump-probe transients were acquired using a 1-kHz CPA Tisapphire laser system delivering 1-mJ pulses with a transform-limited duration (full width at half maximum in intensity) of 38 ± 2 fs and a Wiley–McLaren mass spectrometer. In order to maintain high reliability and reproducibility of data across all molecules, we took great care to maintain crucial experimental parameters, such as laser pulse duration, pulse energy, beam pointing, sample density, and detector bias as close as possible among acquisitions. Occurrence of asymmetric ion yields in our previously published¹⁴ mass spectra were eliminated by employing a circular slit with a diameter of 12.5 mm. Even though this change may have caused an increased volume effect, we did not observe any significant influence on the presented results. All liquid organic samples (with percent purity better than 99.9%) were first dehydrated for more than 24 h using an ample amount of 4-Å molecular sieve desiccants and outgassed using several iterations of freeze-pump-thaw cycles. During all the measurements carried out, the sample gas pressure inside the mass spectrometer was kept at $(3.5 \pm 0.5) \times 10^{-7}$ Torr (corrected for Bayard–Alpert ion gauge sensitivity for the specific gas sample being measured), approximately three orders of magnitude higher than the typical base pressure. The intensity of the pump beam was kept at 2.0×10^{14} W cm⁻² and the probe beam's intensity was set to 1.0×10^{14} W cm⁻². Polarization of the pump beam was kept parallel to the TOF axis and that of the probe was set perpendicular to the pump. No long-lived doubly-charged parent ion, which is the essential precursor state needed for H_3^+ formation, was observed due to ionization by the probe beam. During TOF measurements, all ions produced within the same laser shot were detected using a chevron micro-channel plate (MCP) detector assembly coupled to a 500 MHz, 2 Gsa s⁻¹ digital oscilloscope. The ion detection efficiency of the detector plates was not taken into account since in this configuration, the MCP detection efficiency was shown to exhibit a minimal m/z dependence^{62,63}. Each data point of a given pump-probe transient (e.g. Fig. 4) is an average value of more than 3×10^5 laser shots. The measured signal has an uncertainty lower than 5%.

CTOF data were acquired using a Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS)^{64,65} setup and a CPA Tisapphire laser system, known as PULSAR, operating at 10 kHz repetition rate delivering energies up to 2 mJ per pulse. The pulse duration was measured to be approximately 35 fs during the measurements presented in Fig. 2 and reduced to 23 fs for data shown in Fig. 3. High-purity liquid samples were introduced to the UHV chamber subsequent to thorough outgassing. The laser beam was focused to a peak intensity up to 2.0×10^{14} W cm⁻² (3.0×10^{14} W cm⁻² for CTOF measurements presented in Fig. 3) and directed into a skimmed molecular beam created by a supersonic gas jet, producing doubly-charged parent precursors. The polarization of the incident laser beam was set parallel to the TOF axis. The event rate recorded by the detector was kept below 1 event/shot to reduce random coincidence events. In order to obtain statistically significant results, each acquisition lasted more than 10^8 laser shots. The analytical expression used for the evaluation of total H_3^+ production branching ratios, derived in Supplementary Note 1, is given by

$$F_T(3) = \sum_j F_2(3, j) = \frac{\sum_j M'(3, j)}{\varepsilon \sum_l M_2(l) + \sum_{k \leq j} M'(k, j)}. \quad (2)$$

Observing in some previous published works that the C^{4+} yield at $m/z = 3$ of the mass spectrum had been erroneously assigned to H_3^+ due to degeneracy in m/z , we took extra caution to confirm that there is no contribution from C^{4+} to the ion yield at $m/z = 3$ in our data. In all acquired mass spectra (Supplementary Figs. 1–5), we observed no ions at $m/z = 4$, which can be assigned to C^{3+} , above our detection threshold, an essential precursor for formation of C^{4+} . Thus, we conclude any contribution from C^{4+} yield to our data is insignificant.

Ab initio calculations and simulations. The structural rearrangements following ionization were assessed by performing geometry optimization calculations for the

neutral and the doubly-charged structures of methanol and ethanol at the CCSD/aug-cc-PVDZ level of theory. Mulliken population analysis was carried out at the EOM-CCSD/cc-PVQZ level of theory for both the neutral and doubly-charged electronic configurations of the optimized neutral structures of each alcohol. All CCSD geometry optimizations were carried out using the Molpro 2012.1 software package^{66–68} while the EOM-CCSD property calculations were performed using GAMESS^{69,70}. Ab initio molecular dynamics for the dissociation of doubly-charged ethanol were carried out using the CASSCF method employing 12 electrons in 12 orbitals as an active space. The 6-31G** basis set was used. We have also carried out dynamics simulations using QCISD with the basis set 6-311G**. The validity of QCISD was benchmarked for methanol and compared with our previously reported CASSCF results¹⁴. The trajectories' initial positions and momenta were sampled from the vibrational Wigner distribution for the neutral ground state computed in the harmonic approximation at each of the aforementioned levels of theory. The dynamics were integrated up to 300 fs while utilizing the velocity Verlet integrator with a time step of 0.5 fs. A total of 2000 trajectories was computed for each method. CASSCF trajectories were calculated using a development version of TeraChem^{71–75} while QCISD calculations were carried out using Molpro 2012.1^{76–78}.

Data availability

The data that support the findings of this study are available within the Supplementary Information and upon reasonable request from the corresponding author.

Received: 11 June 2018 Accepted: 6 November 2018

Published online: 05 December 2018

References

- Thomson, J. J. Further experiments on positive rays. *Philos. Mag.* **24**, 209. (1912).
- Tennyson, J. Spectroscopy of H_3^+ : planets, chaos and the Universe. *Rep. Prog. Phys.* **58**, 421 (1995).
- Eland, J. H. D. The origin of primary H_3^+ ions in mass spectra. *Rapid Commun. Mass Spectrom.* **10**, 1560–1562 (1996).
- Furukawa, Y., Hoshina, K., Yamanouchi, K. & Nakano, H. Ejection of triatomic hydrogen molecular ion from methanol in intense laser fields. *Chem. Phys. Lett.* **414**, 117–121 (2005).
- Okino, T. et al. Ejection dynamics of hydrogenmolecular ions from methanol in intense laser fields. *J. Phys. B At. Mol. Opt. Phys.* **39**, S515–S521 (2006).
- Okino, T. et al. Coincidence momentum imaging of ultrafast hydrogen migration in methanol and its isotopomers in intense laser fields. *Chem. Phys. Lett.* **423**, 220–224 (2006).
- Hoshina, K., Furukawa, Y., Okino, T. & Yamanouchi, K. Efficient ejection of H_3^+ from hydrocarbon molecules induced by ultrashort intense laser fields. *J. Chem. Phys.* **129**, 104302 (2008).
- Kraus, P. M. et al. Unusual mechanism for H_3^+ formation from ethane as obtained by femtosecond laser pulse ionization and quantum chemical calculations. *J. Chem. Phys.* **134**, 114302 (2011).
- Schirmel, N., Reusch, N., Horsch, P. & Weitzel, K.-M. Formation of fragment ions (H^+ , H_3^+ , CH_3^+) from ethane in intense femtosecond laser fields—from understanding to control. *Faraday Discuss.* **163**, 461 (2013).
- Kotsina, N., Kaziannis, S. & Kosmidis, C. Hydrogen migration in methanol studied under asymmetric fs laser irradiation. *Chem. Phys. Lett.* **604**, 27–32 (2014).
- Kotsina, N., Kaziannis, S. & Kosmidis, C. Phase dependence of OD^+ , HOD^+ , and H_3^+ ions released from the deuterated dication of methanol under $\omega/2\omega$ laser field irradiation. *Int. J. Mass Spectrom.* **380**, 34–39 (2015).
- Ando, T. et al. Coherent vibrations in methanol cation probed by periodic H_3^+ ejection after double ionization. *Commun. Chem.* **1**, 7 (2018).
- Boran, Y. et al. Dissociative ionization of ethane with femtosecond pulses of radiation. *J. Phys. B At. Mol. Opt. Phys.* **51**, 035003 (2018).
- Ekanayake, N. et al. Mechanisms and time-resolved dynamics for trihydrogen cation (H_3^+) formation from organic molecules in strong laser fields. *Sci. Rep.* **7**, 4703 (2017).
- Townsend, D. et al. The roaming atom: straying from the reaction path in formaldehyde decomposition. *Science* **306**, 1158–1161 (2004).
- Bowman, J. M. & Suits, A. G. Roaming reactions: the third way. *Phys. Today* **64**, 33–37 (2011).
- Bowman, J. M. & Shepler, B. C. Roaming radicals. *Annu. Rev. Phys. Chem.* **62**, 531–553 (2011).
- Bowman, J. M. Roaming. *Mol. Phys.* **112**, 2516–2528 (2014).
- Bowman, J. M. & Houston, P. L. Theories and simulations of roaming. *Chem. Soc. Rev.* **46**, 7615–7624 (2017).
- Houston, P. L. & Kable, S. H. Photodissociation of acetaldehyde as a second example of the roaming mechanism. *Proc. Natl Acad. Sci. USA* **103**, 16079–16082 (2006).

21. Heazlewood, B. R. et al. Roaming is the dominant mechanism for molecular products in acetaldehyde photodissociation. *Proc. Natl Acad. Sci. USA* **105**, 12719–12724 (2008).
22. Li, H. K., Tsai, P. Y., Hung, K. C., Kasai, T. & Lin, K. C. Communication: photodissociation of CH₃CHO at 308nm: observation of H-roaming, CH₃-roaming, and transition state pathways together along the ground state surface. *J. Chem. Phys.* **142**, 0–4 (2015).
23. Maeda, S., Ohno, K. & Morokuma, K. A theoretical study on the photodissociation of acetone: Insight into the slow intersystem crossing and exploration of nonadiabatic pathways to the ground state. *J. Phys. Chem. Lett.* **1**, 1841–1845 (2010).
24. Tsai, P. Y. et al. Roads leading to roam. Role of triple fragmentation and of conical intersections in photochemical reactions: experiments and theory on methyl formate. *Phys. Chem. Chem. Phys.* **16**, 2854–2865 (2014).
25. Nakamura, M. et al. Dynamical, spectroscopic and computational imaging of bond breaking in photodissociation: roaming and role of conical intersections. *Faraday Discuss.* **177**, 77–98 (2015).
26. Lombardi, A. et al. Rovibrationally excited molecules on the verge of a triple breakdown: molecular and roaming mechanisms in the photodecomposition of methyl formate. *J. Phys. Chem. A* **120**, 5155–5162 (2016).
27. Rauta, A. K. & Maiti, B. Roaming mediated nonadiabatic dynamics in molecular hydrogen elimination from propane at 157nm. *Chem. Phys. Lett.* **661**, 83–88 (2016).
28. Grubb, M. P. et al. No straight path: roaming in both ground- and excited-state photolytic channels of NO₃→NO+O₂. *Science* **335**, 1075–1078 (2012).
29. Grubb, M. P., Warter, M. L., Suits, A. G. & North, S. W. Evidence of roaming dynamics and multiple channels for molecular elimination in NO₃ photolysis. *J. Phys. Chem. Lett.* **1**, 2455–2458 (2010).
30. Mebel, A. M. & Bandrauk, A. D. Theoretical study of unimolecular decomposition of allene cations. *J. Chem. Phys.* **129**, 224311 (2008).
31. Brönsted, J. N. Einige bemerkungen über den begriff der Säuren und basen. *Recl. Trav. Chim. Pays-Bas* **42**, 718–728 (1923).
32. Lowry, T. M. The uniqueness of hydrogen. *J. Soc. Chem. Ind.* **42**, 43–47 (1923).
33. Smith, D. The ion chemistry of interstellar clouds. *Chem. Rev.* **92**, 1473–1485 (1992).
34. Smith, D. & Španěl, P. Dissociative recombination of H₃⁺ and some other interstellar ions: a controversy resolved. *Int. J. Mass Spectrom. Ion Process.* **129**, 163–182 (1993).
35. Hogness, T. R. & Lunn, E. G. The ionization of hydrogen by electron impact as interpreted by positive ray analysis. *Phys. Rev.* **26**, 44–55 (1925).
36. Martin, D. W., McDaniel, E. W. & Meeks, M. L. On the possible occurrence of H₃⁺ in interstellar space. *Astrophys. J.* **134**, 1012–1013 (1961).
37. Geballe, T. R. & Oka, T. Detection of H₃⁺ in interstellar space. *Nature* **384**, 334–335 (1996).
38. Oka, T. Observation of the infrared spectrum of H₃⁺. *Phys. Rev. Lett.* **45**, 531–534 (1980).
39. Watson, W. D. Interstellar molecule reactions. *Rev. Mod. Phys.* **48**, 513–552 (1976).
40. Dalgarno, A. & Black, J. H. Molecule formation in the interstellar gas. *Rep. Prog. Phys.* **39**, 573–612 (1976).
41. Herbst, E. & Klempner, W. The formation and depletion of molecules in dense interstellar clouds. *Astrophys. J.* **185**, 505 (1973).
42. Burrows, M. D., Ryan, S. R., Lamb, W. E. & McIntyre, L. C. Studies of H⁺, H₂⁺, and H₃⁺ dissociative ionization fragments from methane, ethane, methanol, ethanol, and some deuterated methanols using electron-impact excitation and a time-of-flight method incorporating mass analysis. *J. Chem. Phys.* **71**, 4931 (1979).
43. Sharma, V. & Bapat, B. Determination of active sites for H atom rearrangement in dissociative ionization of ethanol. *J. Chem. Phys.* **125**, 1–5 (2006).
44. Kushawaha, R. K. & Bapat, B. Fragmentation dynamics of the methanol dication. *Chem. Phys. Lett.* **463**, 42–46 (2008).
45. Ben-Itzhak, I., Carnes, K. D., Johnson, D. T., Norris, P. J. & Weaver, O. L. Fragmentation of CH₄ caused by fast-proton impact. *Phys. Rev. A* **47**, 3748–3757 (1993).
46. Ben-Itzhak, I., Carnes, K. D., Johnson, D. T., Norris, P. J. & Weaver, O. L. Velocity dependence of ionization and fragmentation of methane caused by fast-proton impact. *Phys. Rev. A* **49**, 881–888 (1994).
47. Jochim, B. et al. Rapid formation of H₃⁺ from ammonia and methane following 4MeV proton impact. *J. Phys. B At. Mol. Opt. Phys.* **42**, 091002 (2009).
48. De, S., Rajput, J., Roy, A., Ghosh, P. N. & Safvan, C. P. Formation of H₃⁺ due to intramolecular bond rearrangement in doubly charged methanol. *Phys. Rev. Lett.* **97**, 1–4 (2006).
49. De, S., Roy, A., Rajput, J., Ghosh, P. N. & Safvan, C. P. Dissociation of methanol by ion-impact: breakup dynamics, bond rearrangement and kinetic energy release. *Int. J. Mass Spectrom.* **276**, 43–48 (2008).
50. Pollard, J. E., Johnson, L. K., Lichtin, D. A. & Cohen, R. B. State-selected reactive scattering. I. H₂⁺ + H₂→H₃⁺ + H. *J. Chem. Phys.* **95**, 4877–4893 (1991).
51. Leei, H. S., Drucker, M. & Adams, N. G. Thermal energy reactions of H₃⁺ and H₃O⁺ with a series of small organic molecules*. *Int. J. Mass Spectrom. Ion Process.* **117**, 101–114 (1992).
52. Milligan, D. B., Wilson, P. F., Freeman, C. G., Meot-Ner (Mautner), M. & McEwan, M. J. Dissociative proton transfer reactions of H₃⁺, N₂H⁺, and H₃O⁺ with acyclic, cyclic, and aromatic hydrocarbons and nitrogen compounds, and astrochemical implications. *J. Phys. Chem. A* **106**, 9745–9755 (2002).
53. Band, Y. B. & Freed, K. F. Dissociation processes of polyatomic molecules. *J. Chem. Phys.* **63**, 3382–3397 (1975).
54. Band, Y. B., Freed, K. F. & Kouri, D. J. Half-collision description of final state distributions of the photodissociation of polyatomic molecules. *J. Chem. Phys.* **74**, 4380–4394 (1981).
55. Dantus, M., Rosker, M. J. & Zewail, A. H. Real-time femtosecond probing of 'transition states' in chemical reactions. *J. Chem. Phys.* **87**, 2395–2397 (1987).
56. Herbst, E. & van Dishoeck, E. F. Complex organic interstellar molecules. *Annu. Rev. Astron. Astrophys.* **47**, 427–480 (2009).
57. Charnley, S. B., Kress, M. E., Tielens, A. G. G. M. & Millar, T. J. Interstellar alcohols. *Astrophys. J.* **448**, 232–239 (1995).
58. Olah, G. A., Mathew, T., Prakash, G. K. S. & Rasul, G. Chemical aspects of astrophysically observed extraterrestrial methanol, hydrocarbon derivatives, and ions. *J. Am. Chem. Soc.* **138**, 1717–1722 (2016).
59. Olah, G. A., Shen, J. & Schlosberg, R. H. Electrophilic reactions at single bonds. XI. Hydrogen-deuterium exchange of molecular hydrogen and deuterium in superacids involving isomeric triatomic (hydrogen, deuterium) ⁺ ions. *J. Am. Chem. Soc.* **95**, 4957–4960 (1973).
60. Wang, H. Formation of nascent soot and other condensed-phase materials in flames. *Proc. Combust. Inst.* **33**, 41–67 (2011).
61. Gilaspay, J. D. Highly charged ions. *J. Phys. B* **34**, R93–R130 (2001).
62. Fraser, G. W. The ion detection efficiency of microchannel plates (MCPs). *Int. J. Mass Spectrom.* **215**, 13–30 (2002).
63. Krems, M., Zirbel, J., Thomason, M. & DuBois, R. D. Channel electron multiplier and channelplate efficiencies for detecting positive ions. *Rev. Sci. Instrum.* **76**, 093305 (2005).
64. Dörner, R. et al. Cold Target Recoil Ion Momentum Spectroscopy: a 'momentum microscope' to view atomic collision dynamics. *Phys. Rep.* **330**, 95–192 (2000).
65. Ullrich, J. et al. Recoil-ion and electron momentum spectroscopy. *Reading* **66**, 1463–1545 (2003).
66. Werner, H. J., Knowles P. J., Knizia, G., Manby, F. R. & Schütz, M. Molpro: a general-purpose quantum chemistry program package. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2**, 242–253 (2012).
67. Werner H.-J. et al. MOLPRO, version 2012.1, a package of ab initio programs. <http://www.molpro.net>.
68. Hampel, C., Peterson, K. A. & Werner, H. J. A comparison of the efficiency and accuracy of the quadratic configuration interaction (QCISD), coupled cluster (CCSD), and Brueckner coupled cluster (BCCD) methods. *Chem. Phys. Lett.* **190**, 1–12 (1992).
69. Piecuch, P., Kucharski, S. A., Kowalski, K. & Musiał, M. Efficient computer implementation of the renormalized coupled-cluster methods: the R-CCSD [T], R-CCSD(T), CR-CCSD[T], and CR-CCSD(T) approaches. *Comput. Phys. Commun.* **149**, 71–96 (2002).
70. Wloch, M., Gour, J. R., Kowalski, K. & Piecuch, P. Extension of renormalized coupled-cluster methods including triple excitations to excited electronic states of open-shell molecules. *J. Chem. Phys.* **122**, 214107 (2005).
71. Ufimtsev, I. S. & Martinez, T. J. Quantum chemistry on graphical processing units. 3. Analytical energy gradients, geometry optimization, and first principles molecular dynamics. *J. Chem. Theory Comput.* **5**, 2619–2628 (2009).
72. Titov, A. V., Ufimtsev, I. S., Luehr, N. & Martinez, T. J. Generating efficient quantum chemistry codes for novel architectures. *J. Chem. Theory Comput.* **9**, 213–221 (2013).
73. Fales, B. S. & Levine, B. G. Nanoscale multireference quantum chemistry: full configuration interaction on graphical processing units. *J. Chem. Theory Comput.* **11**, 4708–4716 (2015).
74. Hohenstein, E. G., Luehr, N., Ufimtsev, I. S. & Martínez, T. J. An atomic orbital-based formulation of the complete active space self-consistent field method on graphical processing units. *J. Chem. Phys.* **142**, 224103 (2015).
75. Towns, J. et al. XSEDE: accelerating scientific discovery. *Comput. Sci. Eng.* **16**, 62–74 (2014).
76. Levine, B. G. & Martínez, T. J. Ab initio multiple spawning dynamics of excited butadiene: role of charge transfer. *J. Phys. Chem. A* **113**, 12815–12824 (2009).
77. Levine, B. G., Coe, J. D., Virshup, A. M. & Martínez, T. J. Implementation of ab initio multiple spawning in the Molpro quantum chemistry package. *Chem. Phys.* **347**, 3–16 (2008).

78. Ben-Nun, M. & Martínez, T. J. Ab initio molecular dynamics study of cis–trans photoisomerization in ethylene. *Chem. Phys. Lett.* **298**, 57–65 (1998).

Acknowledgements

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Atomic, Molecular, and Optical Sciences Program under SISGR (DE-SC0002325) and DE-FG02-86ER13491, for the MSU and JRML groups, respectively. The PULSAR laser at JRML was provided by grant DE-FG02-09ER16115 from the same funding agency. B.G.L. acknowledges the National Science Foundation grant CHE-1565634. Computational resources were provided by the Institute for Cyber-Enabled Research (ICER) at Michigan State University. In addition, this work used the Extreme Science and Engineering Discovery Environment (XSEDE) under allocation CHE-140101. XSEDE is supported by the National Science Foundation under Grant ACI-1548562. N.E. acknowledges several valuable suggestions received from Dr. Vadim Lozovoy during the early stages of the experiment and feedback received from Mr. Matthew Michie and Mr. Patrick Pawlaczyk during the manuscript preparation.

Author contributions

N.E. setup and performed the time-of-flight experiments and coordinated the overall project. T.S. lead the CTOF experiments and their analysis. M.N. performed ab initio calculations and molecular dynamics simulations under the guidance of B.G.L. and wrote relevant sections of the manuscript. N.P.W. and B.M.F. provided significant assistance in executing the time-of-flight experiments. Coincidence measurements were performed by T.S., B.K., P.F., B.J., F.Z., K.B., K.R.P., and K.D.C. under the supervision of D.R., A.R., and I.B.-I. CTOF data analysis, as detailed in Supplementary Notes 1 and 2, was conducted by T.S. under the guidance of I.B.-I. Many valuable insights and suggestions were provided by J.E.J. Final analysis, interpretation, and manuscript preparation were carried out by N.E. with contributions from other authors. M.D. conceived and supervised the project. All authors participated in the scientific discussions and in the revisions of the final manuscript.

Additional information

Supplementary Information accompanies this paper at <https://doi.org/10.1038/s41467-018-07577-0>.

Competing interests: The authors declare no competing interests.

Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2018

4.4 Summary and outlook

In this chapter, we studied the bond rearrangement of molecules via isomerization and roaming mechanisms. Specifically, we showed that in various triatomic molecules, isomerization can occur leading to fragmentation channels where the edge atoms form a new molecule. By computing branching ratios, we showed that the likelihood of the bond-rearrangement processes are about the same order of magnitude, at least in the molecules we studied.

In addition, we studied H_3^+ formation from various alcohol molecules, where we suggested that roaming can occur following double ionization. Furthermore, we showed that H_3^+ branching ratio decreases as the length of the carbon chain increases. Finally, we also showed that hydrogen atoms originating from various sites within the ethanol molecule play a role in H_3^+ formation.

In the future, we hope to extend our studies on the various isotopologues of ethanol. Specifically, through more careful analysis, we hope to determine the site-specific branching ratios of the various formation mechanisms of H_3^+ , H_2O^+ , and H_3O^+ .

Chapter 5

Coherent control of molecular ions

In this chapter, we present our results on the coherent control of molecular-ion beams. Specifically, we show that a pump-dump-like transition occurs in CS^{2+} within a single laser pulse due to the potential energy landscape. This is in contrast to conventional pump-dump coherent control, where the pump and dump processes are driven by different laser pulses. We also discuss how such transitions can also be thought of as a delayed Raman transition. In addition, we explore the dissociation of D_2^+ in a two-color field, where we control the emission direction of the D^+ fragment along the laser polarization. We show that the fragmentation of different vibrational states have small phase shifts relative to each other. These phase differences correspond to “time-delays” on the order of 10’s of attoseconds.

5.1 Introduction

Coherent control is a technique that exploits the quantum nature of matter to guide dynamics to favorable outcomes [32–34, 161–176]. Specifically, the idea is based on using light to control quantum interference, which has found applications in chemical dynamics [32, 161–167], photoassociation [168–170], laser cooling [171–173], quantum information [174–176], and more.

There are two dominant methods for trying to coherently control quantum mechanical

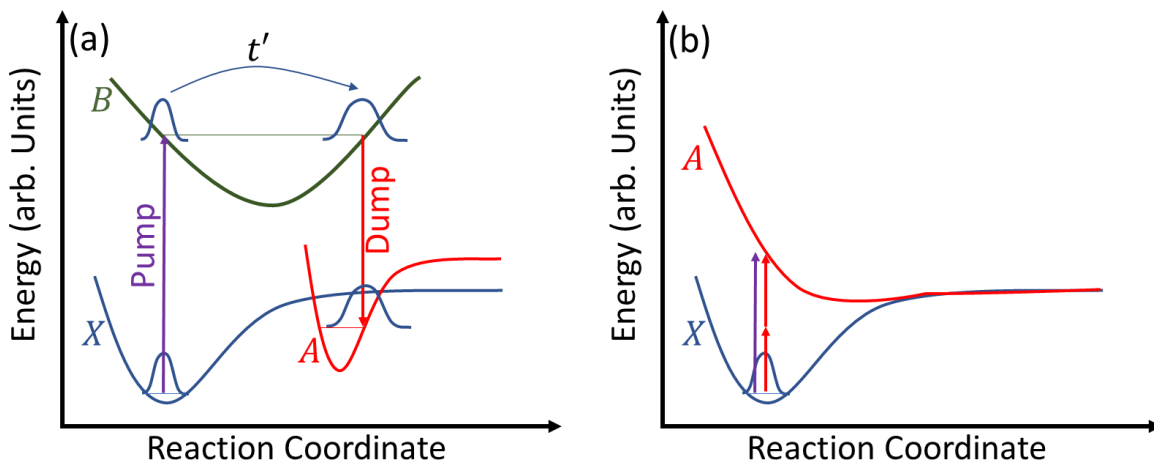


Figure 5.1: Schematic figures demonstrating (a) pump-dump and (b) two-color $\omega - 2\omega$ control.

systems using ultrafast laser pulses. The first technique is also known as feedback control [163, 164], which involves simultaneously controlling many parameters of the electric field using an optimization algorithm to maximize some predetermined outcome, such as a specific fragmentation channel. The strength of this approach is that researchers do not need detailed knowledge about system’s structure to “quickly” maximize a specific outcome. However, if one wants to understand the physical mechanisms of how the shaped electric field leads to the optimal outcome, it is usually difficult to deconvolve the influences of different characteristics of the optimized electric field’s structure. On the other hand, the second approach usually requires detailed knowledge of the system you are trying to control because the laser fields need to be tuned to allow specific transitions. However, the benefit is that the mechanism of control is well understood. Below, we investigate a few prototypical examples of the latter case and explore how it can be accomplished in either the time or frequency domains.

In the time domain, a prototypical example of coherent control is the pump-dump control scheme [34, 161, 164, 168–170], shown schematically in Fig. 5.1(a). Specifically, one pulse is used to project the initial X state into some excited B state, where the resulting wavepacket evolves. At a later time, a second pulse stimulates emission of a photon, de-exciting the system into a lower energy state A . This approach, for example, has been used to induce the isomerization of molecules [177–180]. In Section 5.2, we discuss a pump-dump-like transition

occurring in a CS^{2+} molecular target. In this case, the pump and dump steps occur within the same laser pulse due to the structure of the potential energy curves.

In the frequency domain, one can control dynamics by interfering indistinguishable final states formed by competing pathways [34]. Specifically, by interfering states of the same parity, one may control the yields of certain outcomes [34, 181, 182]. On the other hand, by interfering states with opposite parities, one may observe spatial asymmetries like the emission of a fragment in the forward or backward direction along the laser polarization [34, 45, 183–199]. To control such interferences, researchers manipulate the driving laser fields using, for example, pulse shaping [163, 200, 201], two-color fields [181–190], carrier-envelope phase [45, 191–199], and more. In Fig. 5.1(b), we show an example of two-color $\omega - 2\omega$ control. Specifically, the competing and interfering pathways are due to transitions between the X and A states by either absorbing one photon with energy $2\hbar\omega$ or two photons with energy $\hbar\omega$. Furthermore, since absorbing a photon promotes transitions between states with opposite parities, the two pathways interfere, leading to spatial asymmetries in the forward and backward direction of the laser fields.

In Section 5.4, we present our results on two-color control of D_2^+ dissociation. Here, we interfere opposite parity final states, thus creating spatial asymmetries in the emitted D^+ fragments in the forward and backward directions along the laser polarization. Specifically, we observe phase shifts between the dissociation of different initial vibrational states which correspond to “time delays” on the order of 10’s of attoseconds.

5.2 Pump-dump control mechanism in CS^{2+}

Below, we present a draft of a paper that focuses on the strong-field induced fragmentation of CS^{2+} molecules. Notably, we observe a feature in the KER of the $\text{C}^+ + \text{S}^+$ dissociation channel corresponding to no significant energy gain from the laser field. We attribute this feature to a pump-dump mechanism, where the molecule absorbs a photon and transitions to an excited state where it begins to dissociate. Then, the laser pulse stimulates the emission of a photon when the wavepacket reaches the Condon point with the ground state at

larger R after circumventing its potential barrier, inducing a transition back to the ground state. In this case, the pump and dump steps are driven by the same pulse, contrary to the conventional pump-dump control schemes. Alternatively, one can view this as a Raman transition, where the absorption and stimulated emission of the photon are delayed with respect to one another due to the structure of the potential energy curves. Specifically, the stimulated emission of the photon is energetically forbidden while the molecule is stretching and circumventing the potential energy barrier. We expect such processes to occur in other metastable dicationic molecules which share similar electronic structure due to the asymptotic Coulomb repulsion of the fragments, as we discuss in the paper below for the CO^{2+} molecular-ion beam.

Strong-field dissociation of metastable CS^{2+} molecules by a pump-dump control mechanism within a single laser pulse

T. Severt,^{1, a)} M. Zohrabi,¹ K. J. Betsch,¹ Bethany Jochim,¹ B. Berry,¹ K. D. Carnes,¹ Tereza Uhlíková,² B. D. Esry,¹ and I. Ben-Itzhak^{1, b)}

¹⁾*J.R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506 USA*

²⁾*Department of analytical chemistry, University of Chemistry and Technology, Technick 6, Prague 6, Czech Republic*

(Dated: 7 June 2021)

The strong-field dissociation of a metastable CS^{2+} molecular ion beam is studied using a kinematically complete coincidence three-dimensional momentum-imaging technique. The dominant photodissociation process of CS^{2+} into $\text{C}^+ + \text{S}^+$ involves a single-photon transition between the ground state and first-excited state. Unexpectedly, we also observe dissociation to the same final products without a significant energy gain from the laser field. We attribute this observation to the absorption of a photon, stretching of the molecule, and then stimulated emission of a photon all within the pulse duration of the laser. This process that can be thought of as either a pump-dump-like or delayed Raman transition.

PACS numbers: 32.80.Qk, 34.50.Gb, 42.50.Hz, 33.80.Rv

I. INTRODUCTION

Imaging and controlling molecular dynamics on ultrafast time scales has been the ambition of chemical physicists over the past few decades. Pioneering experiments conducted by Zewail *et al.*^{1,2} imaged the time evolution of molecular dynamics on femtosecond timescales using the pump-probe technique. This technique uses an ultrafast laser pulse to initiate dynamics in the molecule and, at a later time, a probe pulse to further excite and image the evolution of the resulting wavepacket. In recent years, this pump-probe technique has been pushed to attosecond timescales^{3–9}, in hopes of also imaging electronic dynamics.

Another ultrafast technique used to image and/or manipulate molecular dynamics is the pump-dump control scheme, which was first proposed by Tannor, Rice, and Kosloff^{10,11}. This technique is similar to the pump-probe technique except that the dump pulse, whose analog is the probe pulse, de-excites the system through stimulated emission. This technique has been used, for example, to control the photoisomerization of large chiral molecules^{12–14} in the ultrafast regime and to photoassociate molecules¹⁵ in the ultracold regime^{16,17}.

In this paper, we focus on metastable molecular dications, which are part of a family of molecules known as “thermochemically unstable dications,”^{20–22} that is diatomic or polyatomic^{23,24} dications with energy higher than the respective singly charged fragments. Specifically, we study the dissociation of CS^{2+} initiated by an intense ultrafast laser pulse. Such ions present a unique situation where a pump-dump process can occur in a sin-

gle laser pulse because of the electronic structure of the molecule, provided that the pulse is long enough.

According to structure calculations by Šedivcová *et al.*²⁵, the lowest quasibound states of CS^{2+} , specifically the $X^3\Pi$, $A^3\Sigma^-$, $a^1\Pi$, $b^1\Sigma^+$, and $c^1\Delta$ (listed in order of increasing energy), are strongly coupled by the spin-orbit interaction. As a result of the mixing between these states, the singlet states are depleted on a timescale much shorter than the flight time of the CS^{2+} ion to the interaction region. In contrast, low lying vibrational states of the lowest two triplet states, which are strongly mixed by the spin-orbit coupling, live long enough to reach the interaction region. For example, the lifetime of the $v = 7$ vibrational state in the adiabatic electronic ground state including spin-orbit coupling²⁵, is much longer than 10 μs , i.e., longer than the CS^{2+} flight time to the point of interaction with the laser. Given that the laser field does not couple states of different spin multiplets, we only consider the lowest triplet states of CS^{2+} , and show them in Fig. 1 without spin-orbit coupling to simplify the discussion of dissociation pathways involving dipole transitions.

As we demonstrate experimentally below, photodissociation involving a one-photon, $X^3\Pi$ to $A^3\Sigma^-$ transition is the main fragmentation mechanism. Interestingly, we also observe dissociation without significant energy gain from the driving laser field (referred to, hereafter, as “no energy gain” for brevity). We attribute this feature in the measured energy spectrum to a pump-dump mechanism. Alternatively, one may view this as a Raman process in which the stimulated emission is delayed. This phenomenon, i.e., dissociation without significant energy gain from the laser field, is not unique to CS^{2+} but is expected to be common in molecules having any kind of predissociative scenario with a long lifetime.

The signature of this dissociation process, nearly zero energy gain from the field, is reminiscence of “zero-

^{a)}Corresponding author: tsevert@phys.keu.edu

^{b)}Corresponding author: ibi@phys.keu.edu

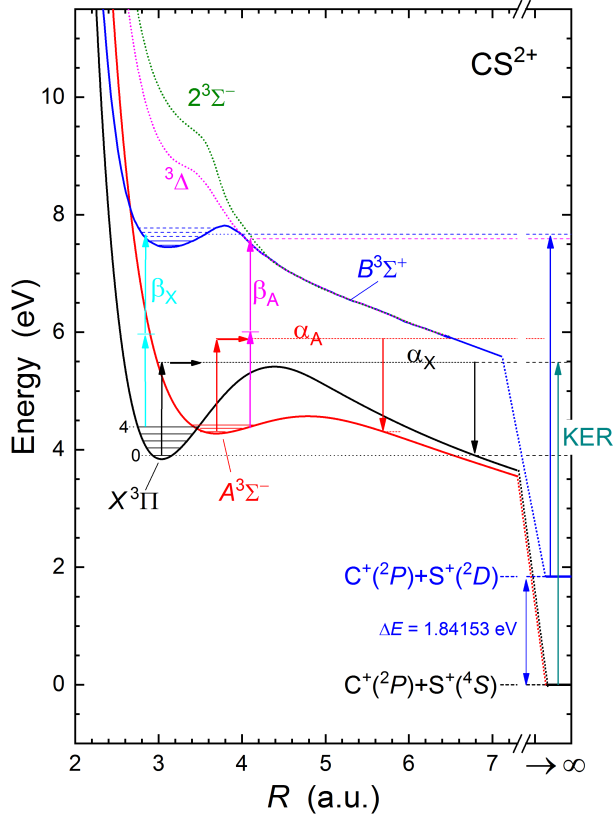


FIG. 1. Potential energy curves of the low-lying triplet states of the CS^{2+} dication with $J=0$ and without spin-orbit coupling (see Sec. II). The energy gap between the lowest dissociation limits, ΔE , was computed using the energy levels reported on the NIST database¹⁸. The arrows represent the 783-nm photons absorbed or emitted in the different dissociation pathways denoted by different colors, and discussed in the text. The vibrational levels shown were computed using a phase-amplitude method¹⁹ (Note that vibrational levels dissociating rapidly, i.e. measured as fragments, are denoted by dashed lines.)

photon dissociation” (ZPD) observed in H_2^+ dissociation^{26–30}, for example, which also involves a two-photon Raman process, however, in that case the stimulated emission is not significantly delayed as is the case in here.

II. THEORETICAL METHOD

The potential energy curves, transition dipole moments, permanent dipole moments and spin-orbit couplings of CS^{2+} , investigated in here, were obtained by extending previous *ab initio* calculations²⁵. Briefly, these were computed (to the same accuracy as in previous work²⁵), using the complete active space self-consistent field (CASSCF) followed by internally-contracted multireference configuration interaction (icMRCI) methods as implemented in the MOLPRO suite of programs³¹. The full valence space consisted of $5\sigma-8\sigma$, 2π and 3π

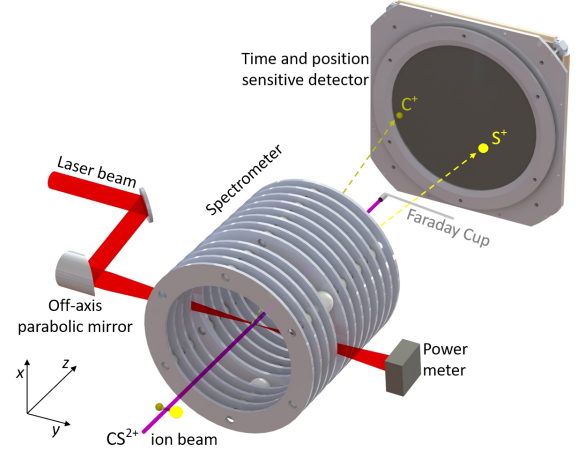


FIG. 2. Schematic view of the experimental setup.

orbitals. The correlation-consistent cc-pV5Z basis set of Dunning and co-workers^{32,33} was used. The spin-orbit integrals were evaluated with the icMRCI wave functions using the Breit-Pauli operator, as implemented in the MOLPRO code.

III. EXPERIMENTAL METHOD

The experiments were conducted using a Ti:Sapphire laser known as PULSAR, which provides 2-mJ, 23-fs Fourier-transform limited (FTL) pulses with a central wavelength of about 783 nm at 10 kHz. The laser beam was focused onto the ion-beam target by an $f=203$ -mm off-axis parabolic mirror, as shown in Fig. 2. The peak intensity at the focus was determined to be $6 \times 10^{15} \text{ W/cm}^2$ by imaging the beam profile with a CCD, characterizing the pulse duration (full width at half maximum (FWHM) in intensity) by a frequency-resolved optical gating (FROG) measurement³⁴, and monitoring the pulse average power during the whole experiment. As most measurements of interest in this work required lower peak intensity than the highest available, specifically $1 \times 10^{14} \text{ W/cm}^2$ was used for the data shown below, the laser focus was set slightly off the ion-beam centerline (i.e. shifted along the laser propagation direction, i.e., the y -axis shown in Fig. 2) to increase the interaction volume with the ion beam. This increased volume, together with the high repetition rate of the laser, enabled a reasonable counting rate (of about 1 Hz) even for the very low target density of the 0.1-nA CS^{2+} beam.

The CS^{2+} beam was produced by fast electron-impact ionization of CS_2 vapor in an electron cyclotron resonance (ECR) ion source. These dications were accelerated to about 24 keV³⁵ and selected by a magnet. Then, the ion beam was collimated by electrostatic lenses and 4-jaw slits, and finally directed through a longitudinal spectrometer toward a small (2-mm diameter) Faraday

cup, which monitors the beam current and protects the imaging detector from the high flux of beam particles, as shown in Fig. 2.

The laser beam crosses the ion beam within the longitudinal spectrometer, which accelerates the resulting ionic fragments such that the less massive fragment, the carbon in our case, always hits the detector first. This detector³⁶ provides time and position information of both fragments, measured in coincidence, which is recorded event-by-event for offline analysis. We use the time and position information to evaluate the momenta of both beam fragments, and momentum conservation is imposed (with $\Delta P \sim \pm 10$ a.u. in each direction, note that $P_z = 11,500$ a.u. in the interaction region) to reject random coincidences. From these momenta, we evaluate the kinetic energy release (KER) upon fragmentation and angular distributions resulting from the laser-molecule interaction. Further details about this coincidence three-dimensional (3D) momentum imaging technique can be found in our previous publications^{37–40}.

IV. CS^{2+} BEAM TARGET PROPERTIES

Before presenting our results, it is important to determine which states of the metastable CS^{2+} are populated upon arrival in the interaction region. Note that these molecular dications arrive at the interaction region after traveling about $15 \mu\text{s}$ from the moment they were created in the ion source. Fast electron impact in the ion source typically creates molecular ions in a multitude of electronic states, with their associated vibrational population given approximately by the Franck-Condon principle, as shown for example in vibrationally resolved measurements on hydrogen molecules^{41,42}. Due to the long flight time, states with shorter lifetimes decay, providing us with a target in a limited number of non-negligibly populated electronic states. For example, McKenna *et al.*⁴³ studied laser-induced dissociation of CO^{2+} overwhelmingly in its ground state [i.e., $X^3\Pi(v=0)$].

Similarly, the CS^{2+} is predominantly in its $X^3\Pi$ electronic ground state when probed by the laser, since the lifetimes of the low lying vibrational states ($v=0-7$) are much longer than $15 \mu\text{s}$. On the other hand, the lifetime of the $a^1\Pi(v=0)$ state, i.e., the lowest lying singlet state, is on the order of $0.8 \mu\text{s}$ (and much shorter for higher vibrational states within the same potential well) due to spin-orbit coupling with lower lying triplet states²⁵. Therefore, the initial population of the $a^1\Pi$ state is suppressed by many orders of magnitude, since its lifetime is much shorter than the flight time to the interaction region. Furthermore, according to the reported²⁵ structure and lifetimes, the only vibrational levels of the CS^{2+} electronic ground state still populated in the interaction region have energies below the $a^1\Pi(v=0)$. Therefore, unimolecular population transfer from these long-lived vibrational states to the $a^1\Pi$ state cannot occur in spite of the strong spin-orbit coupling simply because these

transitions are energetically forbidden. As a result, we can exclude all singlet states from consideration of CS^{2+} laser-induced dissociation as those states have no initial population in the interaction region and the laser field does not couple different spin multiplets.

In contrast, spin-orbit coupling between the $X^3\Pi$ and $A^3\Sigma^-$ states leads to some mixing of these states. Using the spin-orbit coupling between these two states, we estimate that the $A^3\Sigma^-$ state population is of the order of a few percent of the CS^{2+} beam, while the vast majority is in the $X^3\Pi$ ground state. Fortunately, as we discuss in the next section, the initial population in both these states undergoes similar dissociation dynamics without affecting the conclusions one can draw.

Finally, we note that the CS^{2+} molecule in the interaction region is populated in a wide range of vibrational states. Evaluating the vibrational population of CS^{2+} is complicated by the fact that it is produced from CS_2 vapor in the ion source, and therefore the calculation of the Franck-Condon factors is not as straightforward as for molecular ions produced from a diatomic parent molecule. We estimate that only the lower $v=0-4$ vibrational states of the $X^3\Pi$ electronic ground state, shown in Fig. 1, survive all the way to the interaction region, while higher vibrational states predissociate in flight. Likewise, only the $v=0-2$ vibrational states of the $A^3\Sigma^-$ state are probed by the laser.

V. RESULTS AND DISCUSSION

As stated above, we study the metastable CS^{2+} molecule as a representative of a large family of thermochemically unstable molecules. That is, molecules with an energy barrier toward a lower dissociation limit than the initial state. Our main interest is the laser-driven dissociation of these molecules, in which no energy is gained from the strong-laser field, in other words, circumventing the energy barrier to enable dissociation. We show below that the underlying mechanism can be understood in terms of a pump-dump scheme occurring within a single laser pulse, or alternatively as Raman scattering with delayed stimulated emission.

As described in Sec. IV, the CS^{2+} molecule arrives at the interaction region predominantly in the $X^3\Pi(v=0-4)$ state. Based on the potentials shown in Fig. 1, we expect a one-photon excitation of $X^3\Pi(v_i)$ to $A^3\Sigma^-(E)$ vibrational continuum (indicated by a single upward arrow in the figure) to dominate dissociation over the competing two-photon processes. It is worth noting that a one-photon $X^3\Pi$ to $X^3\Pi$ transition made possible by the permanent dipole of this molecule, can dissociate the CS^{2+} leading to the same KER as the $X^3\Pi$ to $A^3\Sigma^-$ transition. Though typically such permanent-dipole driven transitions are hard to observe, we have recently shown that in some cases – like the dissociation of NO^{2+} – they may dominate⁴⁴, and therefore should be considered as a possible contributor. This photodissociation

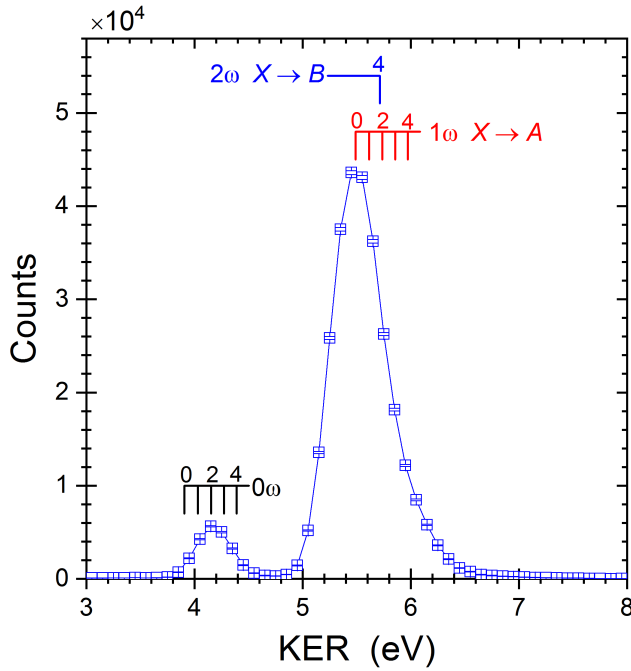


FIG. 3. The KER distribution of CS^{2+} dissociation into $\text{C}^+ + \text{S}^+$ driven by a 23-fs, 1×10^{14} -W/cm², pulse centered about 783 nm. The black, red and blue combs mark expected KER values for net zero-, one- and two-photon transitions from the electronic ground state, respectively. The numbers above the combs indicate the initial vibrational level of the $X^3\Pi$ state for these transitions.

process leads to a kinetic energy release (KER) of around 5.5–6.0 eV, which is in agreement with the prominent $\text{C}^+ + \text{S}^+$ KER peak shown in Fig. 3. We note that the measured KER peak at

~ 5.5 eV matches the expected KER once the experimental resolution⁴⁵ of ~ 0.45 eV at 5.5 eV is included.

The high-energy side of the same KER peak also contains contributions from the two-photon $X^3\Pi(v_i = 4)$ to $B^3\Sigma^+(v = 2)$ transitions (marked by the blue tick mark in Fig. 3), which can occur within the bandwidth (about 80 meV FWHM) of the laser pulse, indicated as pathway β_X in Fig. 1. Similar transitions to lower vibrational states, specifically the $B^3\Sigma^+(v = 0, 1)$, do not contribute because of the long lifetimes ($> 0.9 \mu\text{s}$) associated with tunneling of these states⁴⁶. On the other hand, two-photon absorption leading to the lowest, $\text{C}^+(^2P) + \text{S}^+(^4S)$, dissociation limit, either via $X^3\Pi \rightarrow A^3\Sigma^- \rightarrow X^3\Pi$ dipole transitions or through $X^3\Pi$ to $X^3\Pi$ permanent-dipole transitions, contribute at ~ 7.0 – 7.6 eV, where the yield is very low indicating that these transitions are not very likely.

Now that the dissociation mechanisms responsible for the prominent KER peak in Fig. 3 have been identified, we turn our attention to the more intriguing, smaller KER peak centered about 4.15 eV. As indicated on the figure by the black comb, this peak matches the expected KER for the dissociation of the $X^3\Pi(v_i = 0-4)$ states

without significant energy gain from the laser field, i.e., the net absorption of zero photons. Recall that tunneling, having this KER signature, can be excluded as the lifetimes of these states are very long compared to their flight time through the spectrometer field⁴⁶.

The mechanism responsible for this dissociation without significant energy gain begins with a one-photon excitation from the $X^3\Pi(v_i)$ state to the $A^3\Sigma^-(E)$ vibrational continuum. Then the molecule stretches, circumventing the potential barrier of the $X^3\Pi$ state. Finally, stimulated emission drives an $A^3\Sigma^-(E)$ to $X^3\Pi(v_i)$ transition, which leads to dissociation with the same KER that the initial vibrational state would have if it tunneled through the potential barrier. It is important to note that stimulated emission is energetically forbidden until the molecule stretches, beyond the potential barrier, to the Condon point around 6.8 a.u. for $v = 0$ of the $X^3\Pi$ state, marked by a downward black arrow in Fig. 1. We expect that the stimulated-emission probability, at this point would be higher than at larger internuclear distance because the continuum nuclear wave function on the $X^3\Pi$ state peaks at this point leading to larger Franck-Condon factors. This dissociation pathway, denoted α_X in Fig. 1 is illustrated by up and down black arrows. Finally we note that the possibility of a similar dissociation pathways initiated by a $X^3\Pi(v_i)$ to $X^3\Pi(v_f)$ permanent dipole photoexcitation followed by stimulated emission cannot be excluded. The relative strengths of the two competing pathways depend on the magnitude of the permanent dipole moment as well as the transition dipole couplings, and evaluating this ratio is beyond the scope of this work.

We return to Fig. 3 to draw attention to the fact that one-photon dissociation seems to peak for the lowest vibrational state, $v_i = 0$, while two-photon dissociation with no energy gain from the field is centered about the $v_i = 2$ vibrational state of the $X^3\Pi$. Further work is needed in order to determine the origin of this difference.

The dissociation mechanism suggested above may be described as a pump-dump control^{10,11,14}, a well known coherent-control scheme, but with the difference that a single pulse drives the pump and dump steps instead of two independent pulses. The time delay between the pump and dump steps is determined by the time it takes the molecule to stretch from its equilibrium to the Condon point beyond the potential barrier. We estimate this time delay, using simple classical propagation on the $A^3\Sigma^-$ potential, to be about 38 fs for the lowest vibrational state (and shorter for higher vibrational states). Note that the pulse intensity at that moment needs to be high enough to stimulate the photon emission. Given that one-photon absorption can occur early in our 23-fs intense laser pulse, we expect sufficient intensity to stimulate emission 38 fs after the photoexcitation.

Alternatively, one can envision this dissociation mechanism as a Raman transition, in which the stimulated emission is delayed by a few tens of femtoseconds. Prompt stimulated emission will lead to a long lived

CS^{2+} as the possible vibrational excitation is too small to modify the lifetime significantly. Of course, stimulated emission is energetically forbidden while the molecule traverses over the energy barrier, however once the Condon point is reached stimulated emission may occur leading to dissociation into $\text{C}^+ + \text{S}^+$. As our estimates above indicate, that may result in a significant delay (~ 40 fs) of the stimulated emission step of this Raman scattering.

As mentioned in Sec. IV, a small fraction of the CS^{2+} ions are initially in the $A^3\Sigma^-(v'_i)$ state (with $v'_i = 0-2$). The rate of spin-orbit transition rates²⁵ between the relevant vibrational states of the $X^3\Pi$ and $A^3\Sigma^-$ state is slow enough to neglect them during the laser pulse duration, though they are important on the timescale of the flight time from the ion source and the interaction region. The $A^3\Sigma^-(v'_i)$ states can also undergo a similar pump-dump dissociation scheme (denoted α_A in Fig. 1), starting by one-photon $A^3\Sigma^-(v'_i)$ to $X^3\Pi(E)$ excitation, followed by stretching and finally a stimulated emission, i.e., an $X^3\Pi(E)$ to $A^3\Sigma^-$ transition, around the Condon point at ~ 5.7 a.u. for $v=0$, as marked by a downward red arrow in Fig. 1. Here too, permanent dipole $A^3\Sigma^- \rightarrow A^3\Sigma^- \rightarrow A^3\Sigma^-$ transitions may follow a similar pump-dump dissociation path. This dissociation mechanism contributes to the same low-KER peak centered at 4.15 eV. Finally, two-photon transitions from the $A^3\Sigma^-(v'_i)$ state can lead to the higher dissociation limit, $\text{C}^+(^2P) + \text{S}^+(^2D)$, via the pathway denoted β_A in Fig. 1). These transitions contribute a KER similar to the one associated with the $X^3\Pi(E)$ to $B^3\Sigma^+$ marked by the blue tickmark on that figure.

It is worth noting that the CS^{2+} target we use in this experiment may be rotationally hot due to its production mechanism in the ion source, raising questions about the impact of its angular momentum on the interpretation of our results, which were based on the $J=0$ case. To that end we calculated, using the phase amplitude method¹⁹, the shifts of the vibrational levels and the changes in their lifetimes for $J=10$ and found that the modifications were small. For example the $B^3\Sigma^+(v=2,3)$ states shifted up by about 10 meV and their lifetime are reduced by about 20% (i.e., to 0.8 ns and 0.75 μs), respectively. This provides further credence to the qualitative interpretation of the CS^{2+} dissociation with no energy gain from the laser field as a pump-dump mechanism or a delayed Raman scattering.

We also expect a similar pump-dump mechanism to occur in other metastable (also known as “thermochemically unstable”²²) molecules. For example, we previously observed dissociation of CO^{2+} into $\text{C}^+ + \text{O}^+$ without significant energy gain from the laser field⁴³. In the CO^{2+} case, this process was much smaller in comparison to photodissociation by the absorption of one photon than in the present study of CS^{2+} . In general, the dissociation rate of this pump-dump mechanism and its relative importance with respect to photodissociation by one photon is expected to depend on the structure of the specific molecule and couplings between its lowest states. Nev-

ertheless, we expect this pump-dump dissociation, i.e., fragmentation without energy gain from the laser field, to be prevalent in metastable (thermochemically unstable) molecules.

VI. SUMMARY

Our studies of metastable CS^{2+} dissociation by intense ultrashort laser pulses reveal a dissociation mechanism involving no energy gain from the laser field. This mechanism should be general for metastable molecules, including polyatomic molecules, having an energy barrier toward dissociation. Previous observation of dissociation with net zero photon absorption in metastable CO^{2+} provides further support for the generality of these findings. Thermochemically unstable molecules have the needed potential landscape to facilitate these conditions and enable dissociation without energy gain. This dissociation process, which resembles a pump-dump control scheme but in a single pulse, or alternatively can be viewed as a Raman scattering with a delayed second step, leads to dissociation without significant energy gain from the laser field, i.e., the net absorption of zero photons.

ACKNOWLEDGMENTS

We thank C.W. Fehrenbach for his assistance with the ECR ion source and PULSAR laser and U. Ablikim for assisting with some of the measurements. This project is supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Science, Office of Science, US Department of Energy under award number DE-FG02-86ER13491. TU acknowledges computational resources were provided by the CESNET LM2015042 and the CERIT Scientific Cloud LM2015085, provided under the programme “Projects of Large Research, Development, and Innovations Infrastructures.”

- ¹A. H. Zewail, *The Journal of Physical Chemistry A* **104**, 5660 (2000).
- ²A. H. Zewail, *Science* **242**, 1645 (1988).
- ³M. F. Kling and M. J. Vrakking, *Annual Review of Physical Chemistry* **59**, 463 (2008).
- ⁴F. Krausz and M. Ivanov, *Rev. Mod. Phys.* **81**, 163 (2009).
- ⁵G. Laurent, W. Cao, H. Li, Z. Wang, I. Ben-Itzhak, and C. L. Coker, *Phys. Rev. Lett.* **109**, 083001 (2012).
- ⁶Z. Chang, P. B. Corkum, and S. R. Leone, *J. Opt. Soc. Am. B* **33**, 1081 (2016).
- ⁷F. Calegari, G. Sansone, S. Stagira, C. Vozzi, and M. Nisoli, *Journal of Physics B: Atomic, Molecular and Optical Physics* **49**, 062001 (2016).
- ⁸A. Kaldun, A. Blättermann, V. Stooß, S. Donsa, H. Wei, R. Pazourek, S. Nagele, C. Ott, C. D. Lin, J. Burgdörfer, and T. Pfeifer, *Science* **354**, 738 (2016).
- ⁹K. Ramasesha, S. R. Leone, and D. M. Neumark, *Annual Review of Physical Chemistry* **67**, 41 (2016).
- ¹⁰D. J. Tannor and S. A. Rice, *The Journal of Chemical Physics* **83**, 5013 (1985).
- ¹¹D. J. Tannor, R. Kosloff, and S. A. Rice, *The Journal of Chemical Physics* **85**, 5805 (1986).

- ¹²A. E. Fitzpatrick, C. N. Lincoln, L. J. G. W. van Wilderen, and J. J. van Thor, *The Journal of Physical Chemistry B* **116**, 1077 (2012).
- ¹³K. Hoki, L. González, M. F. Shibl, and Y. Fujimura, *The Journal of Physical Chemistry A* **108**, 6455 (2004).
- ¹⁴M. Shapiro and P. Brumer, *Reports on Progress in Physics* **66**, 859 (2003).
- ¹⁵C. P. Koch and M. Shapiro, *Chemical Reviews* **112**, 4928 (2012).
- ¹⁶J. Weiner, V. S. Bagnato, S. Zilio, and P. S. Julienne, *Rev. Mod. Phys.* **71**, 1 (1999).
- ¹⁷K. M. Jones, E. Tiesinga, P. D. Lett, and P. S. Julienne, *Rev. Mod. Phys.* **78**, 483 (2006).
- ¹⁸https://physics.nist.gov/PhysRefData/ASD/levels_form.
- ¹⁹E. Sidky and I. Ben-Itzhak, *Phys. Rev. A* **60**, 3586 (1999).
- ²⁰S. D. Price, *J. Chem. Soc., Faraday Trans.* **93**, 2451 (1997).
- ²¹S. D. Price, *Phys. Chem. Chem. Phys.* **5**, 1717 (2003).
- ²²D. Schröder and H. Schwarz, *The Journal of Physical Chemistry A* **103**, 7385 (1999).
- ²³W. Koch, G. Frenking, H. Schwarz, F. Maquin, and D. Stahl, *International Journal of Mass Spectrometry and Ion Processes* **63**, 59 (1985).
- ²⁴M. Hochlaf, A. Pilcher-Clayton, and J. Eland, *Chemical Physics* **309**, 291 (2005).
- ²⁵T. Šedivcová, V. Špirko, and J. Fišer, *J. Chem. Phys.* **125**, 164308 (2006).
- ²⁶J. H. Posthumus, J. Plumridge, L. J. Frasinski, K. Codling, E. J. Divall, A. J. Langley, and P. F. Taday, *Journal of Physics B: Atomic, Molecular and Optical Physics* **33**, L563 (2000).
- ²⁷B. Gaire, *Imaging of slow dissociation of the laser-induced fragmentation of molecular ions*, Ph.D. thesis, Kansas State University (2011).
- ²⁸J. McKenna, F. Anis, A. M. Sayler, B. Gaire, N. G. Johnson, E. Parke, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Phys. Rev. A* **85**, 023405 (2012).
- ²⁹N. G. Kling, K. J. Betsch, M. Zohrabi, S. Zeng, F. Anis, U. Ablikim, B. Jochim, Z. Wang, M. Kübel, M. F. Kling, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Phys. Rev. Lett.* **111**, 163004 (2013).
- ³⁰X. Xie, S. Roither, S. Larimian, S. Erattupuzha, L. Zhang, D. Kartashov, F. He, A. Baltuška, and M. Kitzler, *Phys. Rev. A* **99**, 043409 (2019).
- ³¹H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, *et al.*, “Molpro, version 2012.1, a package of *ab initio* programs,” (2012).
- ³²T. H. Dunning, *The Journal of Chemical Physics* **90**, 1007 (1989).
- ³³D. E. Woon and T. H. Dunning, *The Journal of Chemical Physics* **98**, 1358 (1993).
- ³⁴R. Trebino, K. W. DeLong, D. N. Fittinghoff, J. N. Sweetser, M. A. Krumbgel, B. A. Richman, and D. J. Kane, *Review of Scientific Instruments* **68**, 3277 (1997).
- ³⁵(), The beam energy was selected to assure that fragments originating from dissociation with KER up to about 13 eV would hit the 80-mm diameter imaging detector.
- ³⁶RoentDek, “a chevron assembly of microchannel plates coupled to a hex delay line anode from RoentDek Handels GmbH,” <http://www.roentdek.com>.
- ³⁷I. Ben-Itzhak, P. Q. Wang, J. F. Xia, A. M. Sayler, M. A. Smith, K. D. Carnes, and B. D. Esry, *Phys. Rev. Lett.* **95**, 073002 (2005).
- ³⁸P. Q. Wang, A. M. Sayler, K. D. Carnes, J. F. Xia, M. A. Smith, B. D. Esry, and I. Ben-Itzhak, *Phys. Rev. A* **74**, 043411 (2006).
- ³⁹A. M. Sayler, *Measurements of ultrashort intense laser-induced fragmentation of simple molecular ions*, Ph.D. thesis, Kansas State University (2008).
- ⁴⁰I. Ben-Itzhak, in *Fragmentation Processes: Topics in Atomic and Molecular Physics*, edited by C. T. Whelan (Cambridge University Press, Cambridge, 2013).
- ⁴¹F. von Busch and G. H. Dunn, *Phys. Rev. A* **5**, 1726 (1972).
- ⁴²Z. Amitay, A. Baer, M. Dahan, J. Levin, Z. Vager, D. Zajfman, L. Knoll, M. Lange, D. Schwalm, R. Wester, A. Wolf, I. F. Schneider, and A. Suzor-Weiner, *Phys. Rev. A* **60**, 3769 (1999).
- ⁴³J. McKenna, A. M. Sayler, F. Anis, N. G. Johnson, B. Gaire, U. Lev, M. A. Zohrabi, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Phys. Rev. A* **81**, 061401 (2010).
- ⁴⁴B. Jochim, M. Zohrabi, B. Gaire, F. Anis, T. Uhlíková, K. D. Carnes, E. Wells, B. D. Esry, and I. Ben-Itzhak, *Physical Review Research* (2021), submitted.
- ⁴⁵(), The KER resolution scales with $\sqrt{KER}$ in our experimental setup³⁸. We estimate the KER resolution in the present measurement by scaling from a previous measurement of dissociation of vibrationally-cold CO^{2+} molecules⁴³, wherein the instrumental broadening dominated the width of the KER peak.
- ⁴⁶(), Events associated with dissociation in flight to the detector, occurring once the molecule emerges from the spectrometer field, are rejected by the momentum filtering conditions. Therefore, states with lifetimes exceeding about 100 ns do not contribute to the data presented here.

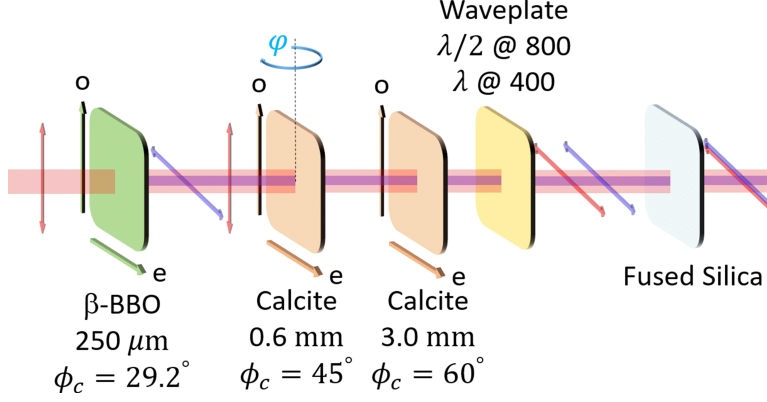


Figure 5.2: The schematic of the two-color generation setup. The angle ϕ represents the rotation angle of the calcite to induce change in the time-delay between the pulses. The angle ϕ_c represents the cut angle of the crystals.

5.3 Two-color control of the dissociation of D_2^+

Here, we describe our two-color control experiment studying D_2^+ dissociation. This study is a follow-up of previous two-color experiments performed by our research group on H_2^+ and its isotopologues, for example see Ref. [105, 202]. We were inspired to revisit this experiment by calculations performed by the theory group of Brett Esry. Specifically, they studied the two-color-driven dissociation dynamics strictly involving the ground state of HeH^+ . In other words, the HeH^+ molecule undergoes vibrational transitions from its ground electronic state to the same state’s vibrational continuum due to its permanent dipole [203, 204]. The important result of their research was a small relative phase shift between the dissociation of different initial vibrational states, which correspond to a “time-delay” on the order of 100’s of attoseconds. This result demonstrated that such “attosecond time-delays” do not necessarily originate from electron dynamics. Although we cannot yet perform an experiment on the HeH^+ ion, our goal is to determine if such “attosecond time-delays” can be experimentally observed. Below, we present our observation of such attosecond time-delays in the dissociation of a D_2^+ ion beam.

To dissociate the D_2^+ molecular ion, we use a two-color 800–400-nm laser field which we generated using the collinear optics setup shown in Fig. 5.2. Specifically, we use an ultrafast linearly polarized pulse from the PULSAR laser, described in Section 2.2, and generate it’s

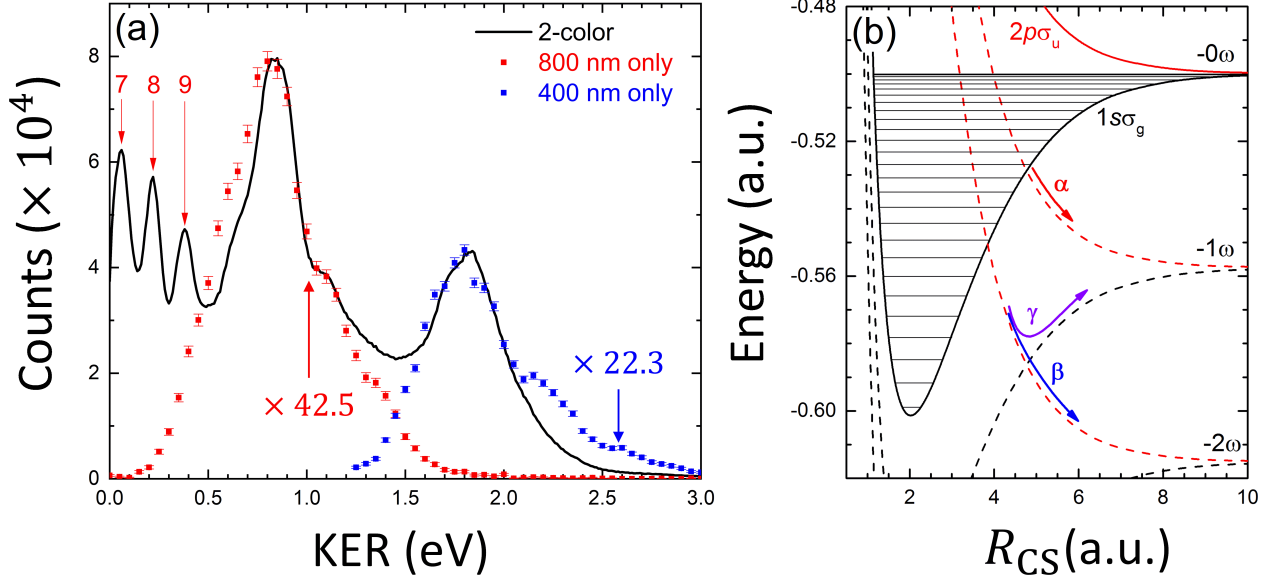


Figure 5.3: (a) The $N(KER)$ distribution for D_2^+ dissociation in the two-color and single-color laser fields. In the two-color case, the $N(KER)$ distribution is integrated over all relative time-delays between the colors. Note that the 800-nm and 400-nm data are scaled to match the peaks in the two-color case. In addition, we cut the 400-nm field contributions below 1.25 eV because of a small contamination of 800-nm light. (b) The two-color fragmentation pathways previously suggested in Ref. [105],

second harmonic using a BBO crystal. We compensate for the group-velocity mismatch between the colors in the downstream optics by employing two calcite plates, where the thin plate is for scanning the phase between the two colors by rotating it in φ while the thick plate is for ensuring that both colors temporally overlap on target, i.e. where the laser intersects the D_2^+ ion beam. Finally, a zero-order waveplate rotates the 800-nm light to have its polarization parallel to the 400-nm light. In this experiment, the intensities of the fundamental and second harmonic are 4×10^{13} and 3×10^{13} W/cm², respectively. The pulse duration of the 800- and 400-nm pulses are measured to be 65 and 80 fs, respectively.

In Fig. 5.3(a), we show the KER distribution of D_2^+ dissociation into $D^+ + D$ for the two-color field and its single-color constituents. The pathways responsible for creating this KER structure, which have been proposed previously [105], are shown in the dressed state potential energy picture in Fig. 5.3(b) and are briefly described below. The 800-nm KER distribution is predominantly due to pathway α , which occurs via bond-softening. It is important to note that the avoided crossing between the $|1s\sigma_g - 0\omega\rangle$ and $|2p\sigma_u - 1\omega\rangle$ states is large enough

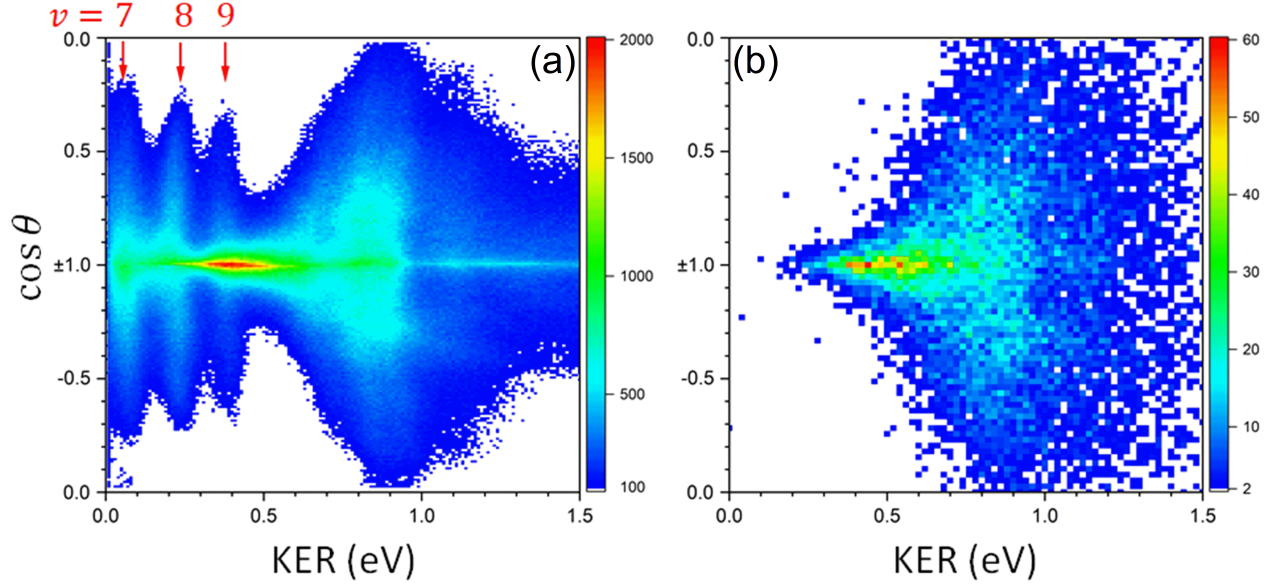


Figure 5.4: The measured $N(\text{KER}, \cos\theta)$ distributions for D_2^+ dissociation for the (a) two-color integrated over all relative time-delays and the (b) 800-nm laser pulses.

for $v = 7$ to dissociate at intensities above 10^{12} W/cm² for the 800-nm field [39, 105]. The 400-nm KER distribution similarly occurs due to bond-softening following pathway β . In the two-color case, both the previous pathways can occur as well as pathway γ , where a 400-nm photon is absorbed followed by the stimulated emission of an 800-nm photon. Pathways α and γ can interfere, leading to a spatial asymmetry about the laser polarization since each pathway ends in an opposite parity state. In addition, three peaks appear at low KER, as shown in Fig. 5.3(a), which we attribute to dissociation originating from the $v = 7 - 9$ vibrational states.

Our data introduces an important question regarding the previously proposed dissociation pathways. Namely, it seems like there is nearly no contribution from pathway α corresponding to the dissociation of $v = 7 - 8$ in the single-color 800-nm case. Furthermore, there is no significant contribution of $v = 9$ for $|\cos\theta| \leq 0.9$, where θ is defined as the angle between the laser polarization and emitted D^+ fragment. To demonstrate this, we show the $N(\text{KER}, \cos\theta)$ distribution for the two-color and single-color 800-nm field in Fig. 5.4(a) and (b)¹, respectively. Since pathway α does not significantly contribute in these regions, it

¹It is important to note that the intensity of the 800-nm pulse used to generate Fig. 5.4(b) is approximately the same as the 800-nm component in the two-color case.

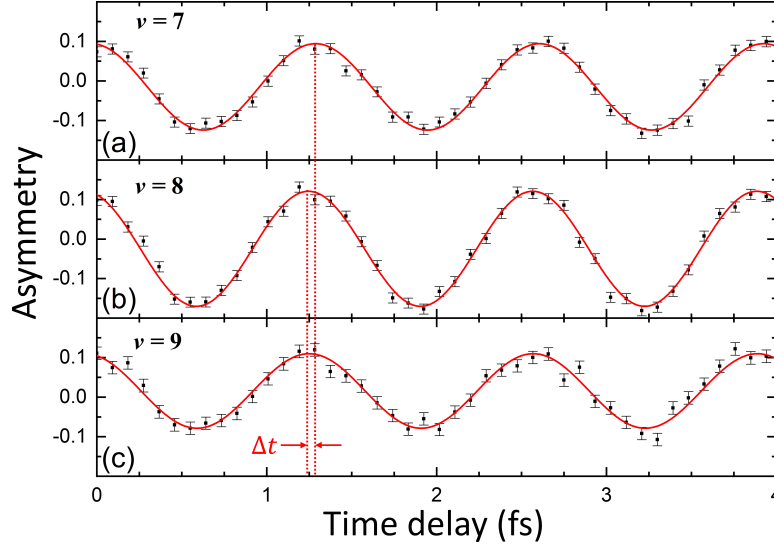


Figure 5.5: *The asymmetry as a function of time-delay between the two-color fields for the (a) seventh, (b) eighth, and (c) ninth vibrational levels.*

suggests that we should not see a two-color interference signal, even though one is clearly visible in Fig. 5.5. Thus, it seems the previously proposed interference between pathways α and γ is inconsistent with our data. We plan to further investigate this open question in the future.

Since the goal of this section is to determine if “attosecond time-delays” can be observed in the dissociation of a molecular-ion beam driven by a two-color field, we continue our discussion of the two-color dissociation of D_2^+ without knowing the exact fragmentation pathways.

In Fig. 5.5, we show the spatial asymmetry as a function of time delay between the 800-nm and 400-nm laser fields for dissociation originating from each vibrational level. Specifically, we calculate the asymmetry as

$$\text{Asymmetry} = \frac{N_f(\text{KER}, \omega\tau) - N_b(\text{KER}, \omega\tau)}{\langle N_f(\text{KER}, \omega\tau) + N_b(\text{KER}, \omega\tau) \rangle_{\omega\tau}}, \quad (5.1)$$

where $N_f(\text{KER}, \omega\tau)$ and $N_b(\text{KER}, \omega\tau)$ represent the number of counts in the forward and

backward direction along the laser polarization², respectively, for specific KER ranges³ and relative phase $\omega\tau$. Note that the sum in the denominator is averaged over all phases to account for any possible phase-dependent oscillations in the yield⁴.

To extract the relative phase shifts in the asymmetry originating from different initial vibrational states, we fit the function:

$$A_v(t) = A_{0,v} \cos(2\omega_0 t + \phi_v) + y_{0,v}, \quad (5.2)$$

where $A_{0,v}$ is the amplitude of the asymmetry of vibrational level v , $2\omega_0$ is the frequency of the second harmonic, ϕ_v is the phase shift, and $y_{0,v}$ is the offset in asymmetry. The relative phase shifts between vibrational levels, i.e. $\Delta\phi_{v,v'} = \phi_v - \phi_{v'}$, are shown in Table 5.1. Note that by fitting over several cycles of the oscillation, we can determine the relative phase shifts to better than the step-size of our measurement. We observe a significant phase shift between dissociation of $v = 7$ and $v = 8$, which corresponds to a “time-delay” of about 51 attoseconds.

Table 5.1: *The relative phase shifts between pairs of vibrational states, $\Delta\phi_{v,v'}$, and the associated time-delays, $\Delta\tau_{v,v'}$.*

v	$\Delta\phi_{v,v'}$	$\Delta\tau_{v,v'} \text{ (as)}$
$7 \rightarrow 8$	0.038 ± 0.005	51 ± 7
$8 \rightarrow 9$	0.006 ± 0.006	8 ± 9
$7 \rightarrow 9$	0.032 ± 0.007	43 ± 9

5.4 Summary and outlook

In this chapter, we explored the coherent control of molecular-ion beams. Specifically, we showed that a CS^{2+} molecule can dissociate with no significant energy gain via a pump-dump mechanism that occurs within a single laser pulse. In addition, we demonstrated

²We integrate over the angular range $0.4 \leq \cos\theta \leq 0.9$ and $-0.9 \leq \cos\theta \leq -0.4$ in the forward and backward directions, respectively.

³The KER regions associated with $v = 7$, 8, and 9 are $0.01 \leq \text{KER} \leq 0.13$, $0.15 \leq \text{KER} \leq 0.28$, and $0.31 \leq \text{KER} \leq 0.44$, respectively.

⁴We also checked for yield oscillations in the data and did not observe any.

two-color control of D_2^+ dissociation, where we measured attosecond time-delays between the dissociation of different initial vibrational levels. This measurement provides support to theory, showing that such small phase shifts, and their associated “attosecond time-delays”, can be experimentally measured.

In the future, we hope to better understand the two-color fragmentation pathways, expand our two-color control measurements to the various isotopologues of H_2^+ , and search for such phase shifts across a single vibrational level. In addition, we plan to extend these two-color control studies to the dissociation of HeH^+ molecules for a one-to-one comparison with theory.

Chapter 6

Enhancing high-order harmonic generation driven by two-color laser fields

6.1 Introduction

This chapter focuses on enhancing high-order harmonic generation (HHG) driven by two-color $\omega - 2\omega$ and $\omega - 3\omega$ laser fields with the goal to produce a higher flux probe for studying molecular dynamics. As stated in the Preface, since this chapter is on a significantly different subject than all other material contained within the thesis, we chose to make this chapter self-contained. Specifically, Section 6.1 provides the necessary background for those less familiar with HHG. Section 6.2 provides a description of the experimental methods used in our research while Sections 6.3 and 6.4 present our results on enhancing HHG using bichromatic driving laser fields presented in a recently submitted paper and a follow up manuscript, respectfully.

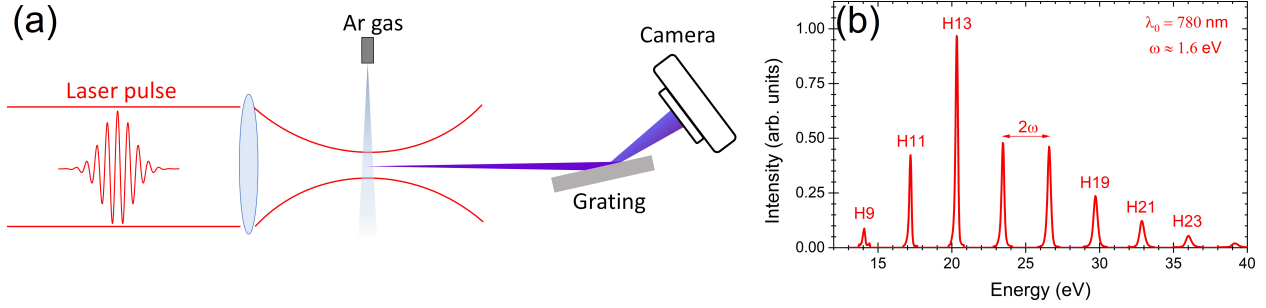


Figure 6.1: (a) A typical setup for HHG from a gas target. (b) An example spectrum of HHG driven by a single color $\lambda_0 = 780\text{-nm}$ laser field. The harmonic orders are labeled in the figure, where the notation *H13* represents harmonic order 13.

6.1.1 What is high-order harmonic generation?

High-order harmonic generation is a method for converting the central wavelength (λ_0) of an intense laser pulse into its higher harmonics, i.e. into λ_0/n where n is an integer that is typically odd [1, 2, 14]. One of the primary uses of HHG is to create vacuum ultraviolet (VUV) to soft X-Ray light that has excellent spatial [205, 206] and temporal coherence [207, 208] properties as well as typical sub-femtosecond pulse durations [209]. The advantage of HHG over other VUV and soft X-ray photon sources, such as free-electron lasers (FELs) [94–96] and synchrotrons [99, 100], is that HHG can be implemented using tabletop setups having low temporal jitter with respect to the driving laser-field and attosecond pulse durations [1, 2, 210, 211], which only the state-of-the-art FEL facilities are beginning to approach [212]. These characteristics make it an important photon source for time resolving nuclear and electron dynamics in varieties of media [29–31, 211, 213]. However, HHG’s low conversion efficiency [1, 2] makes it challenging to produce the peak brilliance achieved at FEL and synchrotron facilities. Therefore, increasing HHG’s conversion efficiency is vital for building a more viable light source.

We show a typical schematic of an HHG setup in Fig. 6.1(a). Briefly, an intense laser beam is focused into an atomic or molecular gas target where the harmonics are generated. It is worth noting that HHG can also occur in liquids [214, 215] and solids [216, 217], though those targets usually restrict the generated photon flux due to strong absorption within the medium. The resulting harmonics are imaged using a spectrometer that contains a

diffraction grating to separate the wavelengths and a camera. Fig. 6.1(b) shows a typical harmonic spectrum produced from an argon target driven by an intense 780-nm laser pulse, which displays only odd-order harmonics. In the next few sections, we describe the physical mechanisms leading to HHG and why it typically only produces odd harmonics.

6.1.2 Three-step model and classical electron trajectories

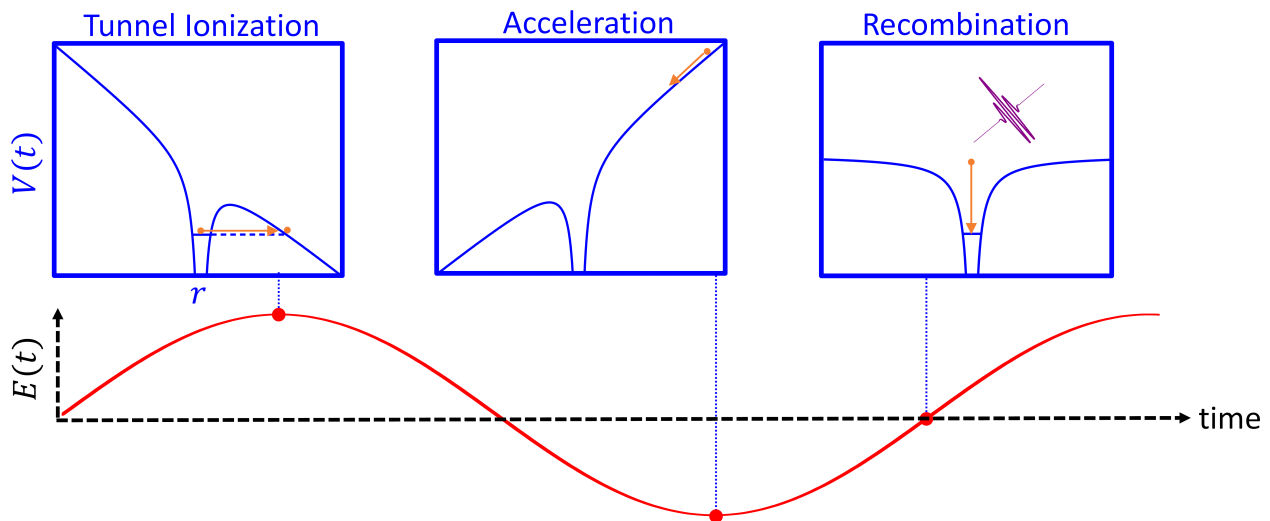


Figure 6.2: A cartoon showing the three-step model. Specifically, the red curve displays the electric field, denoted as $E(t)$, for approximately one cycle of the driving laser pulse. The blue boxes show how the potential energy curve of an atom in an electric field changes at different snapshots in time. Specifically, the potential energy curve is given as $V(t) = 1/r - E(t)r$ in atomic units. This figure was inspired by Ref. [29]

The most prominent model explaining HHG is the three-step model [1, 2, 14, 218–220], which we show schematically in Fig. 6.2. In the first step, the strong electric field tunnel ionizes the target atom (or molecule) and accelerates the photoelectron away from the ion. When the alternating field flips sign, it accelerates the electron back to the remaining ion core, where it may recombine and emit a photon with energy equal to what the electron gained in the field plus the ionization potential of the target. It is worth noting that the photoelectron can also rescatter off the parent ion, creating a highly structured photoelectron momentum distribution containing information about the rescattering wavepacket and the target [2, 17, 221, 222]. This second scenario is beyond the scope of this chapter, however, it

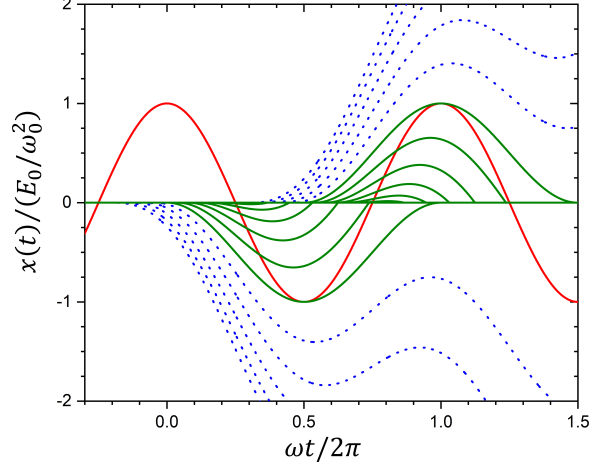


Figure 6.3: The classical electron trajectories in a single-color driving field with central frequency ω_0 . The solid red line represents the electric field $E(t)$ while the solid green lines represent the returning trajectories and the dotted blue lines represent the non-returning trajectories. For typical experimental conditions (laser with central wavelength of $\lambda_0 = 800$ nm and peak intensity of $I_0 = 2.5 \times 10^{14}$ W/cm²), the quantity $E_0/\omega_0^2 \approx 26$ atomic units of length.

is the foundation of the light-induced electron diffraction (LIED) technique used to extract molecular configurations [2, 223–225].

An important consequence of the three-step model is that it provides a semi-classical picture of HHG, where the photoelectron’s journey in the continuum can be easily modeled classically [1, 2, 219]. Considering only one cycle near the peak of a sufficiently long laser pulse (>10 cycles), we can approximate a linearly polarized electric field as $\mathbf{E}(t) = E_0 \cos(\omega_0 t) \hat{\mathbf{x}}$, where E_0 is the amplitude of the field, and ω_0 is its angular frequency. Then, we can solve Newton’s equation of motion in the x direction given by $\ddot{x}(t) = -E_x(t)$, in atomic units, to determine the corresponding electron trajectories. Note that in these calculations, we assume that the electron is released at rest ($\dot{x} = 0$) at an ionization time t_i from the ion core (located at $x = 0$). Also, the electric field due to the Coulomb attraction between the electron and remaining ion is neglected because we assume that the electric field of the laser is much larger than this attraction. The equation describing the electron’s motion in the continuum is

$$\frac{x(t)}{E_0/\omega_0^2} = \cos(\omega_0 t) - \cos(\omega_0 t_i) + \omega_0 (t - t_i) \sin(\omega_0 t_i). \quad (6.1)$$

Some typical trajectories are shown in Fig. 6.3. Specifically, the solid red line shows the electric field, while the dotted blue and solid green lines show the non-returning and returning electron trajectories, respectively. Notice, only a subset of the trajectories return to the ion core at $x = 0$. Furthermore, for a single-color driving field, the trajectories are symmetric in the forward/backward direction every half cycle, suggesting a pulse of light is emitted every half cycle. In the next subsection, we explain how this leads to only odd harmonics.

6.1.3 Odd and even harmonics

To understand why only odd harmonics are observed in Fig. 6.1(b), we consider the interference between two harmonic pulses shifted by half a cycle of the driving field, i.e. $T/2$ (where $T = 2\pi/\omega_0$ is the period of the laser). We write the electric field of the pulses as $E_{tot}(t) = E(t) - E(t - T/2)$, where $E(t)$ describes an arbitrary pulse and the time delayed replica $E(t - T/2)$ is negative because of the opposite sign of the driving electric-field. The Fourier transform of $E_{tot}(t)$ is given by:

$$\mathcal{E}_{tot}(\Omega) = 2\mathcal{E}(\Omega)\sin\left(\frac{\Omega T}{4}\right)\exp\left[i\left(\frac{\pi}{2} - \frac{\Omega T}{4}\right)\right]. \quad (6.2)$$

Then, calculating the spectrum, we find:

$$S(\Omega) = |\mathcal{E}_{tot}(\Omega)|^2 = 4|\mathcal{E}(\Omega)|^2\sin^2\left(\frac{\Omega T}{4}\right), \quad (6.3)$$

which is maximum when the argument of the sin function is $(2q + 1)\pi/2$, where q is an integer. Finally, solving for Ω , one finds that the spectrum peaks at $(2q + 1)\omega_0$, i.e. at odd multiples of the fundamental frequency. Therefore, the interference of multiple pulses separated by half the period of the fundamental driving field leads to odd harmonics.

Before continuing, it is worth noting that even harmonics can be generated. To do so, one must somehow break the symmetry of the pulses generated every half cycle. For example, one can accomplish this by mixing the fundamental field (ω_0) with its second harmonic $2\omega_0$, as has been previously shown [226–229]. Since this chapter also focuses on harmonics

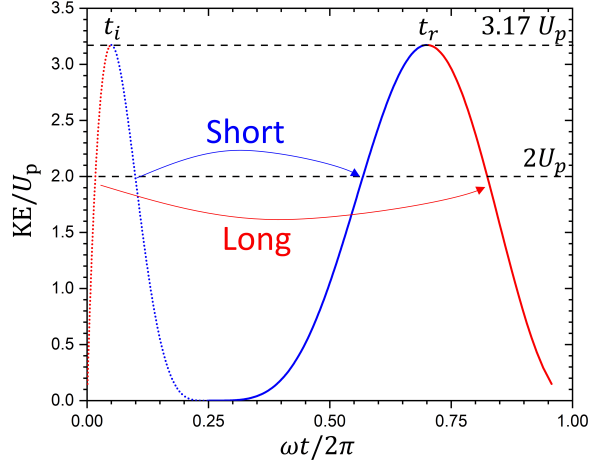


Figure 6.4: The final kinetic energy of the returning photoelectron trajectories as a function of the unitless parameter $\omega t/2\pi$, where t either represents the time of ionization (labeled as t_i and displayed using the dotted lines) or recombination (labeled as t_r and displayed using the solid lines). This plot shows that two trajectories correspond to each return kinetic energy, named the “short” and “long” trajectories based on the length of their excursion times. Finally, this plot also shows that the maximum kinetic energy of the photoelectron is $3.17U_p$.

generated by $\omega - 3\omega$ laser fields, it is worth noting that such fields are symmetric every half cycle and therefore only generate odd harmonics [230, 231].

6.1.4 Short and long electron trajectories

In single-color laser fields, two possible electron trajectories may contribute to each harmonic order. The HHG community has named them the long and short trajectories, which are distinguished by the amount of time the electrons spend in the continuum, i.e. their excursion times [1, 2, 14, 219]. To identify the long and short trajectories, we need to return to the classical model used to calculate the electron trajectories described in Section 6.1.2.

To determine the kinetic energy of the returning electron along each trajectory, we need to numerically solve Eq. 6.1 for the electron’s return time back to the core, t_r , for a given ionization time t_i . We accomplish this by setting $x(t_r) = 0$ and finding all solutions where $t_r > t_i$. With this information, we calculate the electron’s kinetic energy to be

$$\text{KE} = 2U_p [\sin(\omega_0 t_r) - \sin(\omega_0 t_i)]^2, \quad (6.4)$$

where U_p is the pondermotive, i.e. quiver, energy of a free electron in the laser field given by

$$U_p = \frac{E_0^2}{4\omega_0^2}. \quad (6.5)$$

Finally, the expression for the emitted photon energy E_γ is

$$E_\gamma = \text{KE} + I_p, \quad (6.6)$$

where I_p is the ionization potential of the target.

In Fig. 6.4, we show the kinetic energy of the returning electron trajectories as a function of their ionization times t_i (shown as the dotted lines) and their recombination times t_r (shown as the solid lines). To help the reader interpret the figure, we refer to the dotted horizontal black line located at $\text{KE}/U_p = 2$, which twice intersects the t_i and t_r curves, showing that two different electron trajectories contribute to each kinetic energy. These trajectories are named “short” and “long” trajectories based on their excursion times $t_r - t_i$, and are depicted by the blue and red lines, respectively. Specifically, the long trajectory corresponding with $2U_p$ energy is ionized at $\omega_0 t_i / 2\pi \approx 0.017$ and returns at $\omega_0 t_r / 2\pi \approx 0.82$ while the short trajectory is ionized at $\omega_0 t_i / 2\pi \approx 0.10$ and returns at $\omega_0 t_r / 2\pi \approx 0.57$. In the next section, we explain why the short trajectories tend to be favored over the long trajectories.

6.1.5 Micro- and macro-scopic efficiency mechanisms

The efficiency of high-order harmonic generation depends on several mechanisms that lie in two different regimes, the microscopic (i.e. single-atom or molecule) and the macroscopic (i.e. the extended target). To increase the efficiency of HHG, researchers use different schemes to manipulate HHG in these regimes.

Macroscopically, the main mechanism affecting HHG’s efficiency is phase matching [1, 2, 209, 232]. If we consider an extended medium containing many harmonic emitters, the harmonic generation process is considered phase matched when the electric fields radiated

from each emitter add constructively (in phase) at the exit of the medium [233]. To do so, the driving-field and emitted harmonic radiation must traverse the medium at the same group velocity. In reality, this does not occur because the index of refraction of the medium, which influences the speed of light, is frequency dependent. Therefore, the goal is to minimize the phase mismatch between the beams.

The phase mismatch between the driving field and harmonic beams is due to several factors. It is worth mentioning that the textbook by C.D. Lin *et al.* describes all these factors in detail [2]. First is the geometric dispersion, which is related to the focal profile of the laser. For a laser focusing in free space, the geometric dispersion is the Gouy phase shift of a Gaussian beam [234], which can be minimized by placing the target medium “far” from the focus. The second factor is the neutral atom dispersion, which is due to propagation of the driving field and harmonics through the medium. One controls this term by changing the density of the gas. Also, for sufficiently high intensities, this term includes the Kerr effect, which is responsible for self-phase modulation in the medium [233]. The third factor is the free electron or plasma dispersion, which occurs due to the medium’s ionization. It is worth noting that this term has the opposite effect on the phase mismatch than the neutral atom dispersion, meaning that these effects can be tuned to compensate for one another and decrease the total phase mismatch. The final factor is due to the intensity dependent dipole phase of the harmonics, which is related to the phase accumulated by the electron during its excursion in the electric field. Since the accumulated phase is different for short and long trajectories, they are phase matched under different conditions [2]. Typically, the accumulated phase of the long trajectories are difficult to compensate for, therefore making them less efficient than their short trajectory counterparts.

On the microscopic level, HHG can be thought of in the framework of the semi-classical three-step model [1, 2, 14, 218–220]. However, to understand how HHG can be controlled on this level, we need to remember that macroscopically, short trajectories are typically favored over the long trajectories [2]. Furthermore, since the electrons’ excursion is quantum mechanical, their wavepacket’s dispersion (also known as its diffusion) in the continuum also plays a role [220]. Since the long trajectories have longer classical excursion times in

the continuum, they also experience larger amounts of dispersion [220]. Therefore, one can modify HHG’s microscopic efficiency by maximizing the short trajectories’ contributions by controlling the ionization probability associated with the time each trajectory is launched. In addition, the microscopic HHG yield can be further enhanced by minimizing the excursion times, i.e. reducing the electron wavepacket’s diffusion.

It is worth highlighting that, in practice, the microscopic and macroscopic conditions are coupled. For example, one method for reducing the excursion times of trajectories is to make the wavelength of the driving laser field shorter [2, 235]. However, in doing so, many of the phase matching conditions change, resulting in less enhancement than theoretically expected for a single atom or molecule [236]. Therefore, when trying to optimize HHG’s photon flux, one must explore a large parameter space and optimize the source for the various characteristics necessary for each application.

6.1.6 Enhancing HHG’s photon flux

Typically, the conversion efficiency of HHG is on the order of 10^{-5} or smaller [1, 2]. To enhance the total photon flux from HHG, researchers typically explore several methods, usually resorting to a combination of them.

One method is a brute force approach, where researchers develop higher power driving lasers, by either increasing the repetition rates or pulse energies of the driving lasers [209, 237–239], to increase the harmonic photon flux. Alternatively, others try to enhance HHG by focusing on the macroscopic phase matching. Some examples include using a combination of loose focusing geometries and gas cells [240–243], which attempt to maximize the number of atoms/molecules the driving field interacts with while minimizing the phase mismatch. Alternatively, others use gas filled waveguides [232, 244], which can be specially engineered to alter the geometric phase mismatch term and increase HHG’s efficiency [245].

Another approach is to focus on the efficiency at the microscopic level. A popular method is to use mutli-color driving fields [226–231, 246–249], which allows one to modify the electron wavepacket by increasing the ionization rates for the more favorable short electron trajec-

tories [247]. In the past, two-color $\omega - 2\omega$ driving-fields were used with great success. For example, Kim *et al.* [227] used orthogonally polarized 800–400-nm fields to boost harmonics by more than two-orders of magnitude compared to harmonics produced by the 800-nm field alone. Recently, Jin *et al.* [247] theoretically demonstrated that HHG’s efficiency can be improved further by using two-color $\omega - 3\omega$ fields, where the relative phase between the two colors can be tuned to enhance the short trajectory electrons.

In the remaining part of this chapter, we experimentally explore HHG driven by both $\omega - 2\omega$ (800–400-nm) and $\omega - 3\omega$ (800–266-nm) driving laser fields. In these experiments, we minimize phase matching effects by using a thin target gas to help simplify the interpretation of the results. In Section 6.3, we show that 800–266-nm driving fields can enhance HHG by one to three orders of magnitude, depending on the final photon energy, as compared to the fundamental 800-nm field. Furthermore, we show that by changing the relative intensities between these two-color driving fields, we can control whether the ionization rate or the diffusion of the electron wavepacket (via the excursion time of the corresponding electron trajectories) play a larger role in maximizing the HHG flux. In Section 6.4, we compare HHG driven by $\omega - 2\omega$ (800–400-nm) and $\omega - 3\omega$ (800–266-nm) to harmonics generated by their single-color counterparts to determine which scheme provides the largest photon flux for the same input pulse energy into the entrance of the experimental setup.

6.1.7 Classical electron trajectories in $\omega - n\omega$ fields

Since we use classical trajectories to understand HHG’s enhancement in bichromatic fields in Section 6.3, we take a moment to generalize Eq. 6.1 and Eq. 6.4. Writing the bichromatic electric field as $E(t) = E_0 [\cos(\omega_0 t) + \alpha \cos(n\omega_0 t + \phi)]$, where n is the order of the harmonic mixed with the fundamental field, α is the ratio of the amplitude of the harmonic and fundamental electric fields, and ϕ is the relative phase between the fields. The resulting

trajectory is given by:

$$\begin{aligned} \frac{x(t)}{E_0/\omega_0^2} = & \cos(\omega_0 t) - \cos(\omega_0 t_i) + \omega_0(t - t_i) \sin(\omega_0 t_i) \\ & + \frac{\alpha}{n^2} \{ \cos(n\omega_0 t + \phi) - \cos(n\omega_0 t_i + \phi) + n\omega_0(t - t_i) \sin(n\omega_0 t_i + \phi) \}, \end{aligned} \quad (6.7)$$

and the kinetic energy is

$$\text{KE} = 2U_p \left[\sin(\omega_0 t_r) - \sin(\omega_0 t_i) + \frac{\alpha}{n} \{ \sin(n\omega_0 t_r + \phi) - \sin(n\omega_0 t_i + \phi) \} \right]^2. \quad (6.8)$$

It is important to note that these equations reproduce Eq. 6.1 and Eq. 6.4 when $\alpha = 0$, as expected.

6.2 Experimental methods

The experimental methods are explained in detail in the papers and supplementary material to the papers included in Sections 6.3 and 6.4. To reduce repetition, we only briefly describe the method here.

To generate the two-color driving fields, we developed an interferometer where the second (400-nm) or third (266-nm) harmonics of the fundamental (800-nm) laser fields are generated in one of its arms. We chose to generate these harmonics in an arm of the interferometer instead of in front of it because it produced a cleaner wavefront for the 800-nm field, which improved the beam quality of the resulting harmonics. At the exit of the interferometer, the fundamental and second/third harmonic are spatially and temporally recombined and then focused into an argon gas target. The resulting harmonics are then imaged using a spectrometer, similar to the generic schematic shown in Fig. 6.1(a).

There are two aspects of our setup which are unique compared to other more common setups. First, we introduced a channeltron detector near the argon gas jet, allowing us to measure the total ionization rate in the medium. Secondly, we float the interferometer with respect to the optics table to minimize vibrations. This enables the passive stability

between the two arms to have an RMS error of 50 attoseconds. This high stability enables the two-color experiments presented in this chapter.

6.3 Enhancing high-order harmonic generation by controlling the diffusion of the electron wavepacket

In this section, we present our recently submitted paper about enhancing high-order harmonic generation using bichromatic 800 – 266-nm ($\omega - 3\omega$) laser fields. When making this comparison, we take into account that laser systems can only provide a maximum amount of pulse energy. Therefore, we fix the total pulse energy injected into the interferometer in the setup, meaning the two-color fields have lower total pulse energy focused into the target medium compared to the single-color 800-nm field, which uses “all” the energy available. Despite this difference in the total energies, the two-color fields outperform the fundamental field by one to three orders of magnitude.

Secondly, we demonstrate that the bichromatic fields can control whether the ionization rate or the diffusion (dispersion) of the electron wavepacket plays a larger role in enhancing HHG. To show this, we utilize a phase-dependent ionization yield measurement, which maximizes when the bichromatic fields are in phase [250], providing us with an in-situ measurement of the relative phase between the driving fields. Since we are using a thin generation medium, we can relate the phase at which each harmonic is optimized to its corresponding electron trajectories. For an approximately equal intensity ratio, the harmonics’ flux is maximized when the “short” electron trajectories’ excursion times are approximately shortest, i.e. the wavepacket’s diffusion is minimized [220]. On the other hand, for the unequal intensity ratio where the fundamental field is about ten times stronger than the third harmonic, the harmonic flux is maximized when the ionization rate for the “short” trajectories is largest.

Finally, we show that the bichromatic driving-fields produce smaller harmonic divergence angles compared to the 800-nm field. Since the “long” electron trajectories separate in the divergence angle [251–253], this result supports the assertion that we are maximizing

the short over the long trajectories' contribution. Furthermore, by minimizing the long trajectories, we improve the resulting photon beam's wavefront [253], allowing for better refocusing of the beam after the generation medium, increasing the applicability of the light source.

In this project, Jan Tross and I worked together performing the experiments. Specifically, I was responsible for building the two-color interferometer, which enabled these experiments. Jan provided the high-harmonic generation chamber, spectrometer, and the software for acquiring the data, which he developed for other experiments during his Ph.D. I analyzed and interpreted the phase-dependent harmonic data and showed that the harmonic beams' divergence angles were consistent with the interpretation. Jan focused on calculating the enhancements of the two-color driving fields compared to their single-color counterparts. I wrote the draft and prepared the figures of the manuscript with feedback from all coauthors.

Enhancing high-order harmonic generation by controlling the diffusion of the electron wavepacket

T. SEVERT^{1,‡}, J. TROSS^{1,‡}, G. KOLLIPOULOS¹, I. BEN-ITZHAK^{1,*}, AND C. A. TRALLERO-HERRERO^{1,2,**}

¹J.R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA

²Department of Physics, University of Connecticut, Storrs, Connecticut 06269, USA

*Corresponding author: ibi@phys.ksu.edu

**Corresponding author: carlos.trallero@uconn.edu

‡ These authors contributed equally to this work

Compiled June 5, 2021

We experimentally study the enhancement of high-order harmonic generation driven by synthesized $\omega - 3\omega$ laser fields, where we control whether the ionization rate or the electron wavepacket's diffusion is the dominant enhancement mechanism. When minimizing the electron wavepacket's diffusion, the excursion times of the corresponding electron trajectories are reduced by a factor of two or more. This result is important for imaging techniques that use the returning electron wavepacket to probe the remaining ion. Furthermore, we achieve a $10\times$ to $3800\times$ enhancement of the harmonic yield driven by the bichromatic fields relative to that of an optimized single-color field, showing that the bichromatic fields improve HHG's capability as a light source. We also measure that the two-color field's harmonics have half the divergence angle compared to their single-color counterpart, suggesting that the "short" electron trajectories play a more prominent role compared to their "long" trajectory counterparts, thus improving the wavefront of the emerging harmonic beam. © 2021 Optical Society of America

<http://dx.doi.org/10.1364/ao.XX.XXXXXX>

1. INTRODUCTION

Following the strong-field ionization of atoms or molecules, the intense oscillatory electric field of a laser may accelerate the ejected photoelectron back towards the remaining parent ion [1–3]. During the recollision, this photoelectron may, for example, recombine with the parent ion and emit radiation in a process known as high-order harmonic generation (HHG) [4–6] or rescatter off the parent ion, creating a structured high-energy photoelectron spectrum [7, 8]. In each of these cases, the returning electron wavepacket can be used as a probe to study the structure and dynamics of the target immediately following ionization and is the underlying idea of high-harmonic spectroscopy (HHS) [9–19] and laser-induced electron diffraction (LIED) [20–25].

One challenge in using the rescattering electron wavepacket as a probe is that the classical excursion times associated with each trajectory determine when the remaining ion is probed. To tune the excursion times, researchers try to control the returning trajectories by manipulating the ionizing electric fields. For example, Blaga *et al.* [21] controlled the electron trajectories' excursion times by changing their laser's wavelength to probe O₂ and N₂ molecules via LIED. Alternatively, Brugnera *et al.* [26] proposed controlling and enhancing the so-called "long" electron

trajectory contributions in HHG using orthogonally-polarized $\omega - 2\omega$ laser fields, allowing them to probe the remaining ion at different times compared to the "short" trajectories. While both of these examples accomplish the goal of probing the remaining parent ion at different times, it is beneficial to develop alternative methods that take advantage of the dominant short-trajectory electrons and are relatively simple to implement.

In this article, we experimentally demonstrate a method that significantly changes the excursion time of the short-trajectory electrons by controlling the relative phase and intensities of a bichromatic $\omega - 3\omega$ laser-field. Even though our proof-of-principle measurement is demonstrated using HHG from argon, our results should be applicable to any electron rescattering based process since it has been shown that the Coulomb potential of the remaining ion has little effect on the electron trajectories [2, 25, 27].

In addition to HHG's importance as a spectroscopic tool for imaging the structure and dynamics of the target molecule, it also has shown promise as a table-top source of coherent XUV to soft X-ray radiation with attosecond pulse durations [6]. Since its discovery, researchers have investigated various methods to increase the photon flux produced by HHG and improve the beam quality to make it a more viable light source [6, 28–38].

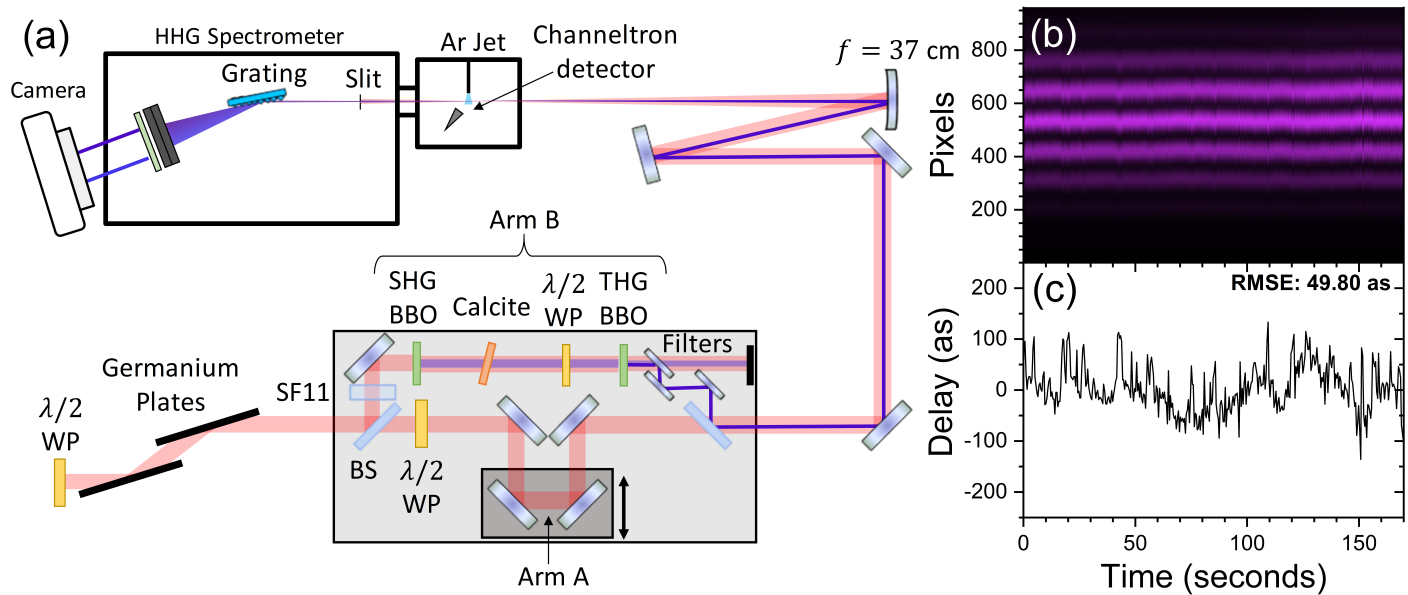


Fig. 1. (a) Schematic of the experimental setup (see text and supplementary information for description). (b) Measured interference pattern of a continuous-wave laser at the output of the interferometer which is used to determine the stability of the interferometer. (c) Fourier analysis of (b) demonstrating a vibrational stability of 49.8 as over 170 seconds without any external feedback to the interferometer. Note that all axes in panels (b) and (c) are plotted using linear scales.

One approach to enhance the photon-flux of HHG based laser sources is to build driving lasers that produce higher pulse energies and repetition rates to generate harmonics [6, 28–30]. An alternative approach is to increase HHG's conversion efficiency, which is typically on the order of 10^{-5} or lower [2, 3]. Many techniques focus on the macroscopic conversion efficiency through improving the phase-matching of HHG [2, 3, 39, 40] either by controlling the plasma defocusing mechanism in the medium [31] or by changing the geometry of the target medium using gas cells [32–34] or gas-filled waveguides [35–38]. Other approaches focus on enhancing the single-atom or molecule conversion efficiency by changing the wavelength of the driving fields [15, 41–45] or using multi-color fields [46–62].

Focusing on multi-color driving fields, Jin *et al.* [58] theoretically proposed using $\omega - 3\omega$ laser fields to enhance the HHG yield by 2 orders of magnitude. Since macroscopic phase matching favors short trajectory electrons, their idea is that bichromatic fields can be tuned to enhance HHG by boosting the ionization rates leading to a subset of electron trajectories which return to the remaining ion and maximize the contributions of the "short" trajectory electrons compared to other competing trajectories.

In this paper, we study the phase-dependent enhancement of HHG driven by two-color 800 – 266-nm laser-fields over their optimized single-color counterparts. When performing this measurement, we chose to fix the input pulse energy since this situation represents the real-world scenario where the output power of the driving laser is limited. In this case, we observe a $10\times$ to $3800\times$ enhancement over the 800-nm field, which is optimized for maximum high-harmonic photon-flux by adjusting its pulse energy and focusing conditions.

Furthermore, we relate the relative two-color phase optimization each harmonic order above the ionization threshold of the target gas to its corresponding electron trajectories by simultaneously measuring the ionization in the target medium. By tuning the relative intensities between the fields, we demonstrate control over whether the quantum diffusion, i.e. dispersion, of

the electron wavepacket or the ionization rate plays a larger role in maximizing the resulting high-order harmonic yield. To our knowledge, this is the first experimental evidence of such control.

Finally, the smaller divergence angle of the enhanced harmonics produced by the two-color fields compared to the 800-nm field supports the assertion that we are optimizing the short over the long trajectories since they can be distinguished in the far-field [26, 63, 64]. More importantly, by optimizing the short trajectories, we improve the wavefront of the resulting photon beam allowing for better refocusing of the emerging harmonic beam after its generation [64], thus increasing the potential applicability of HHG-based light-sources driven by $\omega - 3\omega$ laser-fields.

2. EXPERIMENTAL SETUP

This section briefly describes our experimental setup, shown schematically in Fig. 1(a). We specifically focus on the unique aspects of our setup compared to other standard high-order harmonic generation setups, e.g. see Refs. [60–62] and previous iterations of our own setup described elsewhere [65, 66]. A more complete description of the experimental setup can be found in the supplementary information.

We produce the 800 – 266-nm driving laser-fields using a two-color interferometer, where the third harmonic is generated in a single arm, labeled arm B in Fig. 1(a), using a standard setup of BBOs, calcite, and waveplates [42, 67]. There are several unique features of our interferometer worth noting. First, we tune the dispersion of the 800-nm pulse propagating through arm A, shown in Fig. 1(a), to simultaneously maximize the harmonic yield, cutoff photon energy, and ionization rate in the target gas, creating the shortest pulse possible on target. In other words, we tune the dispersion of that pulse, by adjusting the compressor grating, to compensate for transmission through the waveplate, beamsplitters, air, and entrance window into the vacuum cham-

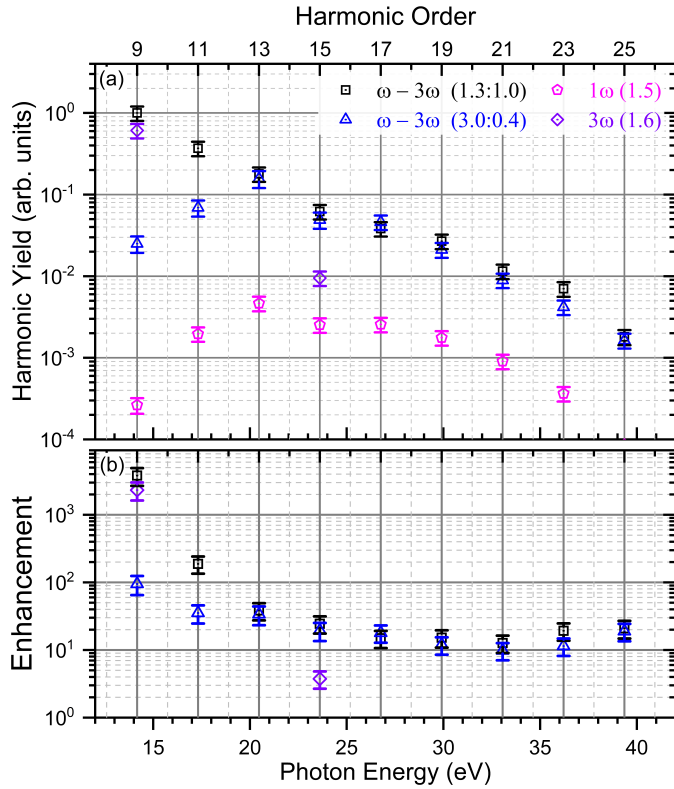


Fig. 2. (a) Harmonic yields driven by ω (pink), 3ω (purple), and $\omega - 3\omega$ for the (3.0:0.4) (blue) and (1.3:1.0) (black) intensity ratios. (b) Enhancement of harmonics generated by the 800 – 266-nm fields over the optimized single-color 800-nm. All graphs are shown as a function of photon energy and harmonic order (top axis). Note that the x axes of these plots are scaled linearly while the y axes are scaled logarithmically.

ber. On the other hand, the 800-nm pulse that traverses arm B has negative dispersion since it does not travel the same optical path. Therefore, to compensate for this negative dispersion and maximize the third harmonic generation, we insert a 2-mm thick SF11 glass plate before the THG setup located in arm B. This way, we minimize the dispersion experienced by each optical path while simultaneously maximizing the third-harmonic conversion efficiency. Secondly, to stabilize the interferometer, we dampen vibrations by isolating the breadboard it is built on from the optical table using mechanical vibration isolation mounts (Newport VIB100). Without any external optical feedback, we measured a RMSE stability of about 50 attoseconds (as) over 3 minutes by imaging the interference pattern of a CW laser. The time-dependent interference pattern is shown in Fig. 1(b) and the resulting phase stability in Fig. 1(c). Given that the optical period of the 266-nm laser-field is approximately 900 as, this high stability enables a two-color phase-control measurement.

We then use the bichromatic field to generate harmonics in a thin argon gas jet, introduced into the vacuum chamber via a glass capillary with an inner diameter of 250 μm , i.e. approximately a factor of 5 less than the Raleigh range of the focused 266-nm laser beam. We use a thin target to minimize volume averaging and propagation effects which would complicate the results' interpretation. In the supplementary information, we include additional details about the beam widths in the gas jet, the position of the gas jet with respect to the focus of the driv-

ing fields, and how we spatially overlap the beams within the generation medium. Finally, we image the generated harmonics using a standard flat-field spectrometer [68]. To determine the optimal conditions for the single- and two-color driving fields, we adjust the focus of the laser with respect to the gas jet to maximize the yield of the plateau harmonics. A sample of raw harmonics spectra, i.e. before applying any efficiency corrections or background subtraction, are included in the supplementary information.

Perhaps most importantly, we simultaneously measure the ionization yield caused by the driving field's interaction with the argon target using a channeltron detector located approximately 2.5 cm from the jet. Specifically, the voltage on the channeltron detector is set to attract the argon ions, with an approximate electric-field strength of 20 V/mm in the interaction region.

3. RESULTS

This section presents our experimental findings for HHG enhancement by 800 – 266-nm laser fields over its single-color counterparts. Specifically, we explore the enhancement for two different intensity ratios, one where the intensity of each color is approximately equal with values of 1.3×10^{14} and 1.0×10^{14} W/cm², respectively, which we refer to as (1.3:1.0) throughout the rest of the paper. The second is an unequal intensity ratio of (3.0:0.4), i.e. a third harmonic intensity of about 10% the fundamental. We observe one to three orders of magnitude of HHG enhancement driven by the two-color fields compared to the single-color 800-nm field.

Furthermore, we exhibit control over whether the ionization rate or electron wavepacket's diffusion is the dominant enhancement mechanism by changing the relative intensity ratios between the two colors. To our knowledge, this is the first experimental demonstration of such control. Finally, the divergence angle of the harmonic beams produced by the two-color fields is generally half of the single-color 800-nm driving field, suggesting that the short trajectories are enhanced compared to the long trajectories.

A. HHG enhancement

For experimentalists, the main limiting factor for increasing the high-harmonic photon flux is the maximum energy per pulse their laser provides, assuming a fixed repetition rate. Therefore, when comparing harmonics produced from the different driving fields, we use the same pulse energies before the interferometer as the single-color 800-nm driving-field's pulse energy. Likewise, for the single-color 266-nm field, we fix the pulse energy at the input of the optics generating the third harmonic. Then, to maximize the overall harmonic yield, we adjust the focusing conditions. It is worth noting that the two-color and single-color fields driving HHG do not have the same pulse energy due to the third harmonic's conversion efficiency, which is about 15% of the 800-nm pulse's energy input into the third harmonic generation's mixing crystals. Nevertheless, we observe significant enhancements in the harmonic yields despite the lower total pulse energy on target of the two-color driving fields. For more information about the input pulse energies, see the supplementary information.

In Fig. 2(a), we plot the harmonics yields for the optimized single color 800- and 266-nm fields as well as for both two-color intensity ratios. These yields are integrated over the divergence angle and bandwidth as well as corrected for each harmonic's detection efficiency (see supplementary information). For the two-

color fields, it is worth noting that the relative phase between the fields is chosen to independently maximize each individual harmonic's yield. Furthermore, Fig. 2(b) shows the enhancement for both intensity ratios of the bichromatic driving-fields and single-color 266-nm field with respect to the single-color 800-nm field. Specifically, we define the enhancement as the integrated photon yield produced by the two-color or 266-nm field divided by the yield of our optimized 800-nm field. We observe that both intensity ratios outperform the optimized 800-nm field by at least one order-of-magnitude.

For photon energies above 20 eV, both two-color intensity ratios approximately enhance the HHG photon yield by about one order-of-magnitude. The main difference between these ratios is observed in the resulting beam's divergence angles, which is further described in subsection C. For photon energies below 20 eV, the approximately equal (1.3:1.0) intensity ratio leads to larger enhancement. Specifically, the 9th and 11th harmonics outperform the single-color driving field by three and two orders-of-magnitude, respectively. It is important to note that the photon energy of the 9th harmonic lies below the ionization threshold of argon at 15.76 eV [69], while the 11th harmonic is located slightly above. It has been shown that resonances can play a prominent role in the generation of below and near threshold harmonics (see the review by Xiong *et al.* [70]). In the case of argon, the 9th harmonic at 14.2 eV lies near several Rydberg states, such as the $3s^23p^5(^1P_{1/2}^o)3d$ state [69], which may help significantly enhance the harmonic's yield. To determine the roles of these resonances, calculations and more careful experiments must be conducted in the future. For our experiment, the difference in enhancement between the two intensity ratios is mainly attributed to the significantly stronger third-harmonic field, which dominates the production of the 9th harmonic as shown for the optimized 266-nm driving field.

B. Phase-dependent HHG yield

To determine the electron trajectories that optimize each harmonic's yield, we perform a two-color phase-dependent measurement of the HHG and ionization yields simultaneously. Specifically, in Fig. 3(a), we show the harmonic yield, integrated over the divergence angles, as a function of the relative phase (time delay) between the colors of the bichromatic 800 – 266-nm laser-field and the photon energy for the approximately equal (1.3:1.0) intensity ratio. Figure 3(c) shows a similar plot, but for the unequal intensity ratio of (3.0:0.4). It is worth noting that in Fig. 3(a&c), we normalize the maximum yield of each harmonic to unity to help visualize the phase dependence. Additionally, the magenta symbols in Fig. 3(a&c) denote when each harmonic is maximized within one period of the oscillations. We also show the associated normalized integrated ion yield for the (1.3:1.0) and (3.0:0.4) intensity ratios in Fig. 3(b). Specifically, we scaled both ionization yields such that the maximum value of the (1.3:1.0) ratio is normalized to unity, demonstrating that the ionization yield is 5.4 times higher for the (3.0:0.4) intensity ratio. For the rest of this section, we focus on interpreting the observed phase-shift between the ionization and the maximum yield of each harmonic.

The phase-dependent total ionization yield provides us with an in-situ measurement of the relative phase between the laser fields because the yield is expected to peak when the two-color fields are in phase [71]. Therefore, since we know the pulses are not significantly chirped from our FROG measurements, we can determine the combined electric field that is expected to contribute most to our observed signals, i.e. near the peak intensity

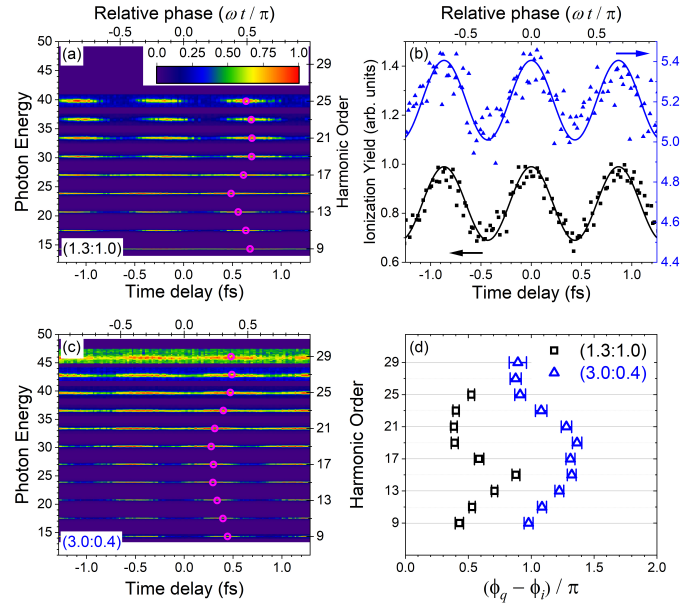


Fig. 3. (a) The measured harmonic yield integrated over divergence angles as a function of the time delay (i.e. relative phase) and the photon energy of the two-color 800 – 266-nm field for the intensity ratio of (1.3:1.0). Note that the maximum amplitude for each harmonic is scaled to unity to help visualize the phase-dependent yield oscillations. The magenta symbols denote the phases at which each harmonic is maximized, as extracted from the fits (see text). (b) The scaled ionization yields as a function of the time delay between the fields for the (1.3:1.0) and (3.0:0.4) intensity ratios, denoted by the black and blue symbols, respectively, are associated with the y axis of the same color. The solid lines display the fits to the data. The data for both intensity ratios are scaled such that the maximum value of the (1.3:1.0) intensity ratio is unity, demonstrating that ionization is a factor of 5.4 higher for the (3.0:0.4) ratio. (c) Same as panel (a), except for an intensity ratio of (3.0:0.4). (d) The extracted phase shifts for each harmonic order (ϕ_q) with respect to the peak ionization yield (ϕ_i) for both intensity ratios. The displayed uncertainty is at the 2σ level. Note that all axes in this figure are scaled linearly.

of the Gaussian envelope of the pulse. With this information, we then unambiguously relate the measured phase corresponding to the maximum harmonic yield to its associated electron trajectories. As we demonstrate in this section, the phase shifts between the maximum harmonic yield and ionization rate suggest that the observed enhancement is not simply due to the increased intensity of the bichromatic field, as the harmonics are not maximized when $\phi_q - \phi_i = 0$.

To determine the relative phase shift between each harmonic order and the peak ionization yield, we fit the function

$$Y_{q,i}(t) = A_{q,i} \cos(3\omega t + \phi_{q,i}) + y_{q,i} \quad (1)$$

to the ionization yield and integrated yield of each harmonic. In the above equation, the subscripts q and i refer to the q^{th} harmonic and the ionization, respectively, ω is the frequency of the fundamental field, $\phi_{q,i}$ is the phase shift, $A_{q,i}$ is the amplitude of the oscillation and $y_{q,i}$ is the yield offset from 0. At this point, it is worth noting that we arbitrarily set the time delay (relative phase) axes in Fig. 3(a-c) such that the extracted ϕ_i is zero. In

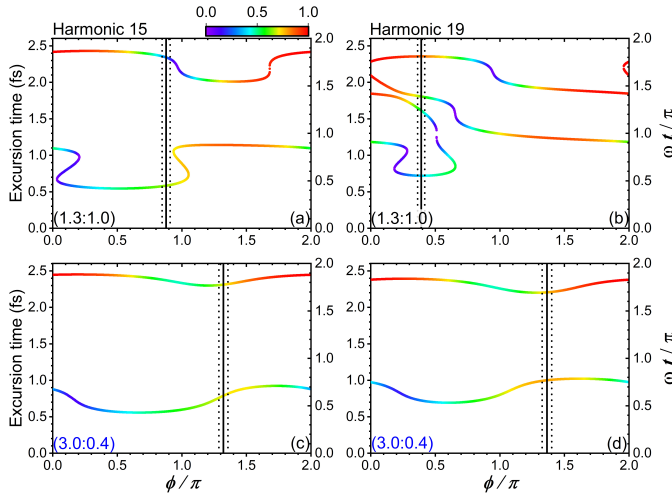


Fig. 4. Excursion times of the classical electron trajectories contributing to the (a) 15th and (b) 19th harmonics, as a function of relative phase between the 800 and 266-nm laser fields for the approximately equal intensity ratio of (1.3:1.0). The color of the lines represent the normalized strength of the electric field at the time of ionization for each trajectory. The solid black vertical lines show the measured phase corresponding to the maximum harmonic yields, while the dotted lines represent the uncertainty (at the 2σ level). Similarly, panels (c) and (d) show the equivalent plots but for an intensity ratio of (3.0:0.4). Note that all axes in this figure are scaled linearly.

Fig. 3(d), we show the extracted phase shifts ϕ_q of each harmonic with respect to the ionization, i.e. $\phi_q - \phi_i$, for both intensity ratios. It is worth mentioning that the line traced by the magenta points in Fig. 3(a&c) appears “flipped” compared to the one shown in Fig. 3(d) due to the time to frequency conversion.

To interpret the observed phase shifts, we must first understand what physical mechanisms affect the HHG yield at the macroscopic and single-atom level. Macroscopically, we employ a thin gas jet (nozzle diameter of 250 μm) to minimize phase mismatching effects along the propagation direction of the laser, such as modification of the driving field due to absorption and dispersion as well as the reabsorption of the generated high harmonics [2, 3, 38–40, 72, 73]. As shown in Refs. [74, 75], ionization provides a natural method for quantitative determination of phase-matching conditions as it is an in-situ measurement of the number of emitters. While not shown here, we routinely check phase matching conditions through the ionization yield and harmonic cutoff. Our conditions are very similar to that of Shiner *et. al.* [74], where they measured the wavelength scaling of HHG’s efficiency at the single-atom level. Therefore, interpreting the phase shift between the maximum ionization and harmonic yields at the single-atom level should be a reasonable approximation under our experimental conditions.

At the single atom level, HHG can be explained using the three-step model [27, 76, 77], where an electron is ionized, accelerated in the laser field, and then recombines with the parent ion emitting a photon. Furthermore, from the quantum mechanical strong-field approximation (SFA), i.e. the Lewenstein model [27], we know that the main mechanisms influencing the harmonic yield are the ionization rate and the electron wavepacket’s dispersion while traversing the continuum, which appears like a classical excursion time within the expression for the time-

dependent dipole (see supplementary information for further discussion). It is worth noting that within this model, the recombination probability is independent of the electric field as long as the ionization of the medium is small enough to not deplete the ground state. Furthermore, it is important to note that the classical electron trajectories are approximately equivalent to the trajectories predicted using SFA (Lewenstein model) within the saddle-point approximation [3, 27]. Therefore, our simulations referred to throughout the rest of the paper show the classical trajectories, which are calculated using the standard approach for two-color fields [2] and are explained further in the supplementary information. We also only focus on the short trajectory electrons because the diffusion of the wavepacket and the macroscopic phase matching favors them over the long trajectories, especially when the focus is located before the target gas jet [2, 39], as is the case in our experiment. It is important to note that the explanations given above (in this paragraph) are only applicable to the harmonics with photon energies above the ionization potential of the argon target. Therefore, in this section, we only focus on the phase dependence of those harmonics.

Figure 4(a-b) shows the excursion times of the possible trajectories returning within one cycle of the fundamental field leading to the central photon energies of the 15th and 19th harmonics, as a function of the relative phase between the two-color laser fields for the intensity ratio of (1.3:1.0). The measured phase $\phi_q - \phi_i$ that optimizes each harmonic is marked by the solid black vertical lines and the line colors correspond to the electric field strength normalized to its maximum possible value when the two-color fields are in phase. Interestingly, each harmonic exhibits complicated phase-dependent structure in the “short” trajectories, i.e. trajectories with excursion times shorter than 1.5 fs. For example, the 15th harmonic trajectory’s excursion times, shown in Fig. 4(a), change by about a factor of 2. Specifically, we find that the excursion time changes from 0.54 fs at $\phi = 0.5\pi$ to 1.15 fs at 1.3π . Notably, the measured harmonic yield is maximized when the trajectory’s excursion time is approximately shortest instead of when the electric field strength, and hence the ionization, is largest. This result suggests that the wavepacket’s diffusion has the largest influence on enhancing each harmonic’s yield. It is important to note that in the region where the excursion time is shortest, i.e. from about $0 - \pi$ for the 15th harmonic, the experimentally measured phase optimizing the harmonic yield shifts to the right side of the region where the electric field strength is stronger. In other words, the phase corresponds to a “goldilocks zone” where the combination of the relatively large ionization rate and the smaller quantum diffusion lead to the maximum harmonic yield. We observe similar behavior for the other harmonics, but show only the 15th and 19th harmonics for brevity.

For the unequal (3.0:0.4) intensity ratio in Fig. 4(c), we show the corresponding phase-dependent trajectories as previously explained for the 15th harmonic. It is important to note that the other harmonics follow similar trends, where we show harmonic 19 as an example in Fig. 4(d). Surprisingly, this intensity ratio exhibits a strikingly different behavior compared to the equal intensity ratio. For example, the short trajectories’ excursion times do not change as much, only changing from about 0.56 fs at $\phi = 0.75\pi$ to about 0.92 fs at 1.7π for the 15th harmonic. Also, the maximized harmonic yield picks out the phases near where the ionization rate for that trajectory is maximized, though slightly shifted towards shorter excursion times.

Our experimental results demonstrate that tuning the intensity ratio of the bichromatic driving field allows one to control

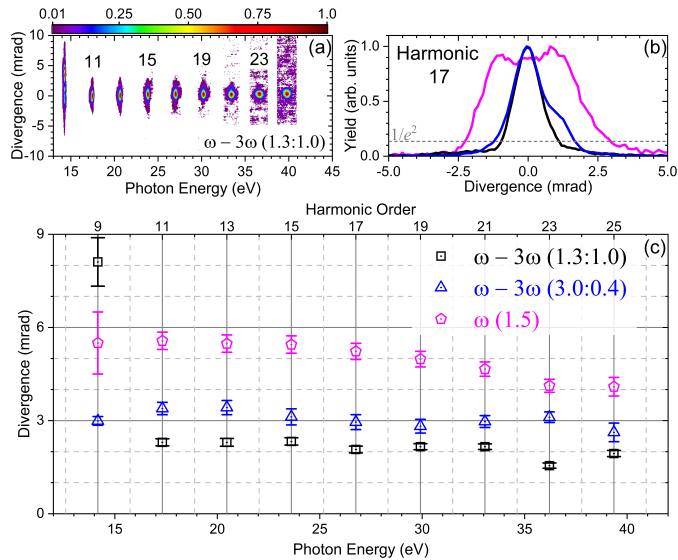


Fig. 5. (a) Photon yield as a function of the photon energy and divergence angle for the intensity ratios (1.3:1.0). Several harmonic orders are marked on the figure for clarity. (b) The integrated yield of the 17th harmonic as a function of its divergence angle for the single- and two-color laser fields, normalized so the maximum value is set to unity. The color coding follows the legend in panel (c). (c) Measured full width divergence angle at $1/e^2$ of the maximum intensity of each harmonic order for the single- and two-color driving fields. Note that all axes in these plots are scaled linearly.

whether the ionization rate when the wavepacket is launched or the wavepacket's diffusion while traversing the continuum has a larger influence over enhancing the harmonic yield. Furthermore, by tuning the relative phase between the fields with an intensity ratio of (1.3:1.0), we control the dispersion of the wavepacket on attosecond time scales, changing the excursion times of the electrons by a factor of two or more. This significant control over the electron's excursion times is applicable to various methods that rely on the timing of the rescattering electron wavepacket to probe the system's dynamics.

Finally, and perhaps most importantly, this control over the rescattering electron wavepacket is expected to be independent of the fundamental wavelength of the driving $\omega - 3\omega$ laser field. Therefore, by going to fundamental fields with longer central wavelengths, the change in excursion times can be further increased, providing researchers with a broader range of recollision times to probe the remaining ion.

It is worth noting that our phase-dependent results suggest a means to increase the resulting harmonics' yield by finding intensity ratios that maximize the ionization rates at phases for which the excursion time of the "short" electron trajectories is the shortest. Hopefully, by exploring this further and combining it with other enhancement techniques that exploit different phase matching mechanisms, like using gas cells [32–34] or waveguides [35–38], the larger enhancements theoretically predicted by Jin *et al.* [58] may be reached.

C. HHG divergence

Studying HHG's divergence is important in measuring the harmonic beam's wavefront quality. Since the accumulated dipole phase for the short and long trajectories have different intensity

dependencies [78–80], each trajectory's contribution is maximized for different phase matching conditions [2, 64]. Focusing on the harmonic's divergence, the spatial intensity profile of the laser leads to the long and short trajectories separating spatially in the far-field, where the long trajectories typically have a larger divergence angle than the short trajectories [26, 63, 64]. This separation in the far-field gives rise to chromatic aberrations [64, 81, 82], which affect the spatial quality and wavefront of the refocused harmonic beam. Therefore, to minimize the aberrations, it is beneficial to minimize the contributions of the long trajectories both on the macroscopic and single-atom level. In our experiment, we placed the focus of all driving fields before the target gas jet, thus minimizing the contributions of the long trajectories [2, 39]. Furthermore, theoretical work by Jin *et al.* [58] suggests that two-color driving fields may further decrease the contributions of the long trajectories. To explore if this is the case, we compare the divergence of the bichromatic fields to the single-color 800-nm field.

In Fig. 5, we show the measured divergence of the harmonics generated by the bichromatic and single-color driving fields. In particular, Fig. 5(a) shows the measured harmonic spectrum as a function of the photon energy and divergence angle for the 800 – 266-nm driving fields for the (1.3:1.0) intensity ratio. Note that the relative-phase between the two-color field chosen as the average of the phases shown in Fig. 3(d) for this intensity ratio. It is important to note that each harmonic's maximum value in Fig. 5(a) is scaled to unity to help visualize the divergence better. In Fig. 5(b), we compare the yields of the 17th harmonic as a function of divergence angle for both two-color intensity ratios as well as the single-color 800-nm driver. From this plot, it is clear that the bichromatic fields significantly outperform the 800-nm driving field.

To quantitatively compare the divergence of each harmonic order, in Fig. 5(c) we plot the measured full width divergence angle at $1/e^2$ of the maximum intensity as a function of harmonic order for the bichromatic and single-color driving fields. For the harmonics produced by the two-color fields, we plot the divergence angle at the phase where each harmonic's flux is maximized. One can see that, for most harmonic orders, the bichromatic fields produce less divergent beams than the 800-nm field. This result is consistent with the assertion by Jin *et al.* [58] that HHG by $\omega - 3\omega$ fields enhances the short over the long trajectories. Furthermore, the (1.3:1.0) intensity ratio produces smaller divergence harmonics than the (3.0:0.4) ratio, with the exception of the 9th harmonic. This result may arise from the difference in excursion times of the electron trajectories for each intensity ratio, though this calls for further investigation. It is important to note that the 9th harmonic may have a significantly different divergence angle due to contributions of resonances [70] in argon [69], as discussed in subsection A.

It is worth noting that there are two other conditions of our experiment that also may assist in minimizing the divergence of the generated harmonics. First, since we are generating the third harmonic in one arm of the interferometer instead of before the interferometer, we eliminated the wavefront distortions in the 800-nm beam due to depletion during the third harmonic generation process. Secondly, as discussed in the supplementary information, the beam diameter of the third harmonic is about 75% the size of the diameter of the fundamental beam. As a result, we are spatially selecting the central portion of the fundamental driving field, which may also assist in minimizing the divergence of the harmonics by decreasing the contributions generated further off axis.

To reiterate the important message of this subsection, the bichromatic fields produce harmonic beams with smaller divergences due to minimizing the contributions of the long trajectories. Since the short and long trajectories have different wavefronts and phases, minimizing the long trajectories allows the resulting beams to have better wavefronts, improving focusing quality and brightness of the photon source.

4. CONCLUSION AND OUTLOOK

We explored the phase-dependent enhancement of high-order harmonic generation driven by $\omega - 3\omega$ laser fields for two different intensity ratios, namely when the intensities are approximately equal (1.3:1.0) and significantly different (3.0:0.4). By measuring the phase-dependent harmonic spectrum and ionization yields simultaneously, each harmonic's phase dependence is related to its corresponding electron trajectories. Then, one can control whether the ionization rate or the electron wavepacket's diffusion plays the dominant role in enhancing HHG by tuning the intensity ratios and relative phase between the two colors. Furthermore, for the (1.3:1.0) intensity ratio, the recolliding electron's classical excursion time is changed by a factor of two or more. Finally, we show that the enhancement and divergence of HHG driven by the bichromatic fields compared to the 800-nm field produce brighter harmonics (by 1-3 orders of magnitude) and less divergent beams (by a factor of two).

Our results are applicable to a wide variety of situations in strong-field induced rescattering physics. While the HHG's enhancement may be unique to our specific experimental conditions, the significant change in the electron's classical excursion times as a function of relative phase is independent of the driving-field's wavelengths. Therefore, we expect similar results for a variety of bichromatic driving-fields, as long as the intensity ratio is properly selected. In addition, the relative-phase-dependent change in the electron's excursion time has the potential to control when the returning electron wavepacket probes the remaining ion, which is crucial in high-harmonic spectroscopy and laser-induced electron diffraction techniques.

One may improve upon our results by exploring other phase-matching media, such as gas cells and waveguides, or by finding the optimal intensity ratios that simultaneously maximize the ionization rates and minimize excursion times of the short trajectories. Also, the improved divergence of the harmonic beams produced by the $\omega - 3\omega$ fields indicates that the long electron trajectory contributions are significantly suppressed, therefore improving the beam's spatial and temporal qualities, which can be beneficial for spectroscopy, coherent imaging, and industrial metrology applications [64].

Funding. This work and T.S. were partially supported by the National Science Foundation under Award No. IIA-1430493. JRML personnel and operations were supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office for Science, U.S. Department of Energy under Award # DE-FG02-86ER13491. C.A. T-H was partially funded by Award # DE-SC0019098 from the same funding agency. The HITS laser was mainly financed by NSF-MRI grant No. 1229672, with additional contributions from DOD-DURIP grant No. FA2386-12-1-3014 and DOE grant No. DE-FG02-86ER13491.

Acknowledgment. We would like to acknowledge Cheng Jin and C.D. Lin for inspiring us to pursue this research. Furthermore, we would like to thank Bincheng Wang and C.D. Lin for

useful discussions about the strong field approximation model for high-order harmonic generation. We would also like to thank K.D. Carnes for assistance with the final manuscript.

Disclosures. The authors declare no conflicts of interest.

See Supplement 1 for supporting content.

REFERENCES

1. C. J. Joachain, N. J. Kylstra, and R. M. Potvliege, *Atoms in Intense Laser Fields* (Cambridge University Press, 2009).
2. Z. Chang, *Fundamentals of Attosecond Optics* (CRC Press, 2011).
3. C. D. Lin, A.-T. Le, C. Jin, and H. Wei, *Attosecond and Strong-Field Physics* (Cambridge University Press, 2018).
4. K. Midorikawa, "High-order harmonic generation and attosecond science," *Jpn. J. Appl. Phys.* **50**, 090001 (2011).
5. V. V. Strelkov, V. T. Platonenko, A. F. Sterzhantov, and M. Y. Ryabikin, "Attosecond electromagnetic pulses: generation, measurement, and application. generation of high-order harmonics of an intense laser field for attosecond pulse production," *Physics-Uspekhi* **59**, 425 (2016).
6. C. M. Heyl, C. L. Arnold, A. Couairon, and A. L'Huillier, "Introduction to macroscopic power scaling principles for high-order harmonic generation," *J. Phys. B: At. Mol. Opt. Phys.* **50**, 013001 (2017).
7. D. D. Hickstein, P. Ranitovic, S. Witte, X.-M. Tong, Y. Huismans, P. Arpin, X. Zhou, K. E. Keister, C. W. Hogle, B. Zhang, C. Ding, P. Johnsson, N. Toshima, M. J. J. Vrakking, M. M. Murnane, and H. C. Kapteyn, "Direct visualization of laser-driven electron multiple scattering and tunneling distance in strong-field ionization," *Phys. Rev. Lett.* **109**, 073004 (2012).
8. W. Becker, S. P. Goreslavski, D. B. Milošević, and G. G. Paulus, "The plateau in above-threshold ionization: the keystone of rescattering physics," *J. Phys. B: At. Mol. Opt. Phys.* **51**, 162002 (2018).
9. J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pépin, J. C. Kieffer, P. B. Corkum, and D. M. Villeneuve, "Tomographic imaging of molecular orbitals," *Nature* **432**, 867 (2004).
10. S. Baker, J. S. Robinson, C. A. Haworth, H. Teng, R. A. Smith, C. C. Chirilă, M. Lein, J. W. G. Tisch, and J. P. Marangos, "Probing proton dynamics in molecules on an attosecond time scale," *Science* **312**, 424 (2006).
11. B. K. McFarland, J. P. Farrell, P. H. Bucksbaum, and M. Guhr, "High harmonic generation from multiple orbitals in N_2 ," *Science* **322**, 1232–1235 (2008).
12. D. Shafir, Y. Mairesse, D. M. Villeneuve, P. B. Corkum, and N. Dudovich, "Atomic wavefunctions probed through strong-field light-matter interaction," *Nat. Phys.* **5**, 412 (2009).
13. O. Smirnova, Y. Mairesse, S. Patchkovskii, N. Dudovich, D. Villeneuve, P. Corkum, and M. Y. Ivanov, "High harmonic interferometry of multi-electron dynamics in molecules," *Nature* **460**, 972 (2009).
14. H. J. Wörner, J. B. Bertrand, D. V. Kartashov, P. B. Corkum, and D. M. Villeneuve, "Following a chemical reaction using high-harmonic interferometry," *Nature* **466**, 604 (2010).
15. A. D. Shiner, B. E. Schmidt, C. Trallero-Herrero, H. J. Wörner, S. Patchkovskii, P. B. Corkum, J.-C. Kieffer, F. Legare, and D. M. Villeneuve, "Probing collective multi-electron dynamics in xenon with high-harmonic spectroscopy," *Nat. Phys.* **7**, 464 (2011).
16. P. M. Kraus, B. Mignolet, D. Baykushcheva, A. Rupenyan, L. Horný, E. F. Penka, G. Grassi, O. I. Tolstikhin, J. Schneider, F. Jensen, L. B. Madsen, A. D. Bandrauk, F. Remacle, and H. J. Wörner, "Measurement and laser control of attosecond charge migration in ionized iodoacetylene," *Science* **350**, 790 (2015).
17. M. Lein, "Molecular imaging using recolliding electrons," *J. Phys. B: At. Mol. Opt. Phys.* **40**, R135 (2007).
18. S. Haessler, J. Caillat, and P. Salières, "Self-probing of molecules with high harmonic generation," *J. Phys. B: At. Mol. Opt. Phys.* **44**, 203001 (2011).
19. J. P. Marangos, "Development of high harmonic generation spectroscopy of organic molecules and biomolecules," *J. Phys. B: At. Mol. Opt. Phys.* **49**, 132001 (2016).

20. M. Meckel, D. Comtois, D. Zeidler, A. Staudte, D. Pavicic, H. C. Bandulet, H. Pepin, J. C. Kieffer, R. Dörner, D. M. Villeneuve, and P. B. Corkum, "Laser-induced electron tunneling and diffraction," *Science* **320**, 1478–1482 (2008).
21. C. I. Blaga, J. Xu, A. D. DiChiara, E. Sistrunk, K. Zhang, P. Agostini, T. A. Miller, L. F. DiMauro, and C. D. Lin, "Imaging ultrafast molecular dynamics with laser-induced electron diffraction," *Nature* **483**, 194 (2012).
22. B. Wolter, M. G. Pullen, A.-T. Le, M. Baudisch, K. Doblhoff-Dier, A. Sentfleben, M. Hemmer, C. D. Schröter, J. Ullrich, T. Pfeifer, R. Moshhammer, S. Gräfe, O. Vendrell, C. D. Lin, and J. Biegert, "Ultrafast electron diffraction imaging of bond breaking in di-ionized acetylene," *Science* **354**, 308–312 (2016).
23. K. Amini, M. Sclafani, T. Steinle, A.-T. Le, A. Sanchez, C. Müller, J. Steinmetz, L. Yue, J. R. M. Saavedra, M. Hemmer, M. Lewenstein, R. Moshhammer, T. Pfeifer, M. G. Pullen, J. Ullrich, B. Wolter, R. Moszynski, F. J. G. de Abajo, C. D. Lin, S. Gräfe, and J. Biegert, "Imaging the Renner–Teller effect using laser-induced electron diffraction," *Proc. Natl. Acad. Sci.* **116**, 8173 (2019).
24. F. Brausse, F. Bach, F. Krečinić, M. J. Vrakking, and A. Rouzée, "Evolution of a molecular shape resonance along a stretching chemical bond," *Phys. Rev. Lett.* **125**, 123001 (2020).
25. C. D. Lin, A.-T. Le, Z. Chen, T. Morishita, and R. Lucchese, "Strong-field rescattering physics—self-imaging of a molecule by its own electrons," *J. Phys. B: At. Mol. Opt. Phys.* **43**, 122001 (2010).
26. L. Brugnera, D. J. Hoffmann, T. Siegel, F. Frank, A. Zair, J. W. G. Tisch, and J. P. Marangos, "Trajectory selection in high harmonic generation by controlling the phase between orthogonal two-color fields," *Phys. Rev. Lett.* **107**, 153902 (2011).
27. M. Lewenstein, P. Balcou, M. Y. Ivanov, A. L'Huillier, and P. B. Corkum, "Theory of high-harmonic generation by low-frequency laser fields," *Phys. Rev. A* **49**, 2117 (1994).
28. E. Takahashi, Y. Nabekawa, and K. Midorikawa, "Generation of 10- μ j coherent extreme-ultraviolet light by use of high-order harmonics," *Opt. Lett.* **27**, 1920 (2002).
29. S. Hädrich, J. Rothhardt, M. Krebs, S. Demmler, A. Klenke, A. Tünnermann, and J. Limpert, "Single-pass high harmonic generation at high repetition rate and photon flux," *J. Phys. B: At. Mol. Opt. Phys.* **49**, 172002 (2016).
30. I. Makos, I. Orfanos, A. Nayak, J. Peschel, B. Major, I. Lontos, E. Skantzakis, N. Papadakis, C. Kalpouzos, M. Dumergue, S. Kühn, K. Varju, P. Johnsson, A. L'Huillier, P. Tzallas, and D. Charalambidis, "A 10-gigawatt attosecond source for non-linear xuv optics and xuv-pump-xuv-probe studies," *Sci. Reports* **10**, 3759 (2020).
31. H.-W. Sun, P.-C. Huang, Y.-H. Tzeng, J.-T. Huang, C. D. Lin, C. Jin, and M.-C. Chen, "Extended phase matching of high harmonic generation by plasma-induced defocusing," *Optica* **4**, 976 (2017).
32. Y. Tamaki, J. Itatani, Y. Nagata, M. Obara, and K. Midorikawa, "Highly efficient, phase-matched high-harmonic generation by a self-guided laser beam," *Phys. Rev. Lett.* **82**, 1422 (1999).
33. J. R. Sutherland, E. L. Christensen, N. D. Powers, S. E. Rhynard, J. C. Painter, and J. Peatross, "High harmonic generation in a semi-infinite gas cell," *Opt. Express* **12**, 4430 (2004).
34. P. Rudawski, C. M. Heyl, F. Brizuela, J. Schwenke, A. Persson, E. Mansten, R. Rakowski, L. Rading, F. Campi, B. Kim, P. Johnsson, and A. L'Huillier, "A high-flux high-order harmonic source," *Rev. Sci. Instruments* **84**, 073103 (2013).
35. A. Rundquist, C. G. Durfee, Z. Chang, C. Herne, S. Backus, M. M. Murnane, and H. C. Kapteyn, "Phase-matched generation of coherent soft x-rays," *Science* **280**, 1412 (1998).
36. T. Pfeifer, R. Kemmer, R. Spitzenpfeil, D. Walter, C. Winterfeldt, G. Gerber, and C. Spielmann, "Spatial control of high-harmonic generation in hollow fibers," *Opt. Lett.* **30**, 1497 (2005).
37. A. Paul, E. Gibson, X. Zhang, A. Lytle, T. Popmintchev, X. Zhou, M. Murnane, I. Christov, and H. Kapteyn, "Phase-matching techniques for coherent soft x-ray generation," *IEEE J. Quantum Electron.* **42**, 14–26 (2006).
38. T. Popmintchev, M.-C. Chen, A. Bahabad, M. Gerrity, P. Sidorenko, O. Cohen, I. P. Christov, M. M. Murnane, and H. C. Kapteyn, "Phase matching of high harmonic generation in the soft and hard x-ray regions of the spectrum," *Proc. Natl. Acad. Sci.* **106**, 10516 (2009).
39. P. Balcou, P. Salières, A. L'Huillier, and M. Lewenstein, "Generalized phase-matching conditions for high harmonics: The role of field-gradient forces," *Phys. Rev. A* **55**, 3204 (1997).
40. L. Harel, G. Shoulga, and A. Bahabad, "Phase matching and quasi-phase matching of high-order harmonic generation—a tutorial," *J. Phys. B: At. Mol. Opt. Phys.* **53**, 233001 (2020).
41. S. Adachi, T. Horio, and T. Suzuki, "Generation of intense single-order harmonic pulse in the vacuum ultraviolet region using a deep ultraviolet driving laser," *Opt. Lett.* **37**, 2118 (2012).
42. D. Popmintchev, C. Hernández-García, F. Dollar, C. Mancuso, J. A. Pérez-Hernández, M.-C. Chen, A. Hankla, X. Gao, B. Shim, A. L. Gaeta, M. Tarazkar, D. A. Romanov, R. J. Levis, J. A. Gaffney, M. Foord, S. B. Libby, A. Jaron-Becker, A. Becker, L. Plaja, M. M. Murnane, H. C. Kapteyn, and T. Popmintchev, "Ultraviolet surprise: Efficient soft x-ray high-harmonic generation in multiply ionized plasmas," *Science* **350**, 1225 (2015).
43. H. Wang, Y. Xu, S. Ulonska, J. S. Robinson, P. Ranitovic, and R. A. Kaindl, "Bright high-repetition-rate source of narrowband extreme-ultraviolet harmonics beyond 22 eV," *Nat. Commun.* **6**, 7459 (2015).
44. C. Marceau, T. J. Hammond, A. Y. Naumov, P. B. Corkum, and D. M. Villeneuve, "Wavelength scaling of high harmonic generation for 267 nm, 400 nm and 800 nm driving laser pulses," *J. Phys. Commun.* **1**, 015009 (2017).
45. S. Adachi and T. Suzuki, "UV-driven harmonic generation for time-resolved photoelectron spectroscopy of polyatomic molecules," *Appl. Sci.* **8**, 1784 (2018).
46. S. Watanabe, K. Kondo, Y. Nabekawa, A. Sagisaka, and Y. Kobayashi, "Two-color phase control in tunneling ionization and harmonic generation by a strong laser field and its third harmonic," *Phys. Rev. Lett.* **73**, 2692 (1994).
47. U. Andiel, G. D. Tsakiris, E. Cormier, and K. Witte, "High-order harmonic amplitude modulation in two-colour phase-controlled frequency mixing," *EPL (Europhysics Lett.)* **47**, 42 (1999).
48. E. Cormier and M. Lewenstein, "Optimizing the efficiency in high order harmonic generation optimization by two-color fields," *The Eur. Phys. J. D - At. Mol. Opt. Plasma Phys.* **12**, 227 (2000).
49. I. Kim, C. Kim, H. Kim, G. Lee, Y. Lee, J. Park, D. Cho, and C. Nam, "Highly efficient high-harmonic generation in an orthogonally polarized two-color laser field," *Phys. Rev. Lett.* **94**, 243901 (2005).
50. L. E. Chipperfield, J. S. Robinson, J. W. G. Tisch, and J. P. Marangos, "Ideal waveform to generate the maximum possible electron recollision energy for any given oscillation period," *Phys. Rev. Lett.* **102**, 063003 (2009).
51. G. Lambert, J. Gautier, C. P. Hauri, P. Zeitoun, C. Valentin, T. Marchenko, F. Tissandier, J. P. Goddet, M. Ribiere, G. Rey, M. Fajardo, and S. Sebban, "An optimized kHz two-colour high harmonic source for seeding free-electron lasers and plasma-based soft x-ray lasers," *New J. Phys.* **11**, 083033 (2009).
52. L. Brugnera, F. Frank, D. J. Hoffmann, R. Torres, T. Siegel, J. G. Underwood, E. Springate, C. Froud, E. I. C. Turcu, J. W. G. Tisch, and J. P. Marangos, "Enhancement of high harmonics generated by field steering of electrons in a two-color orthogonally polarized laser field," *Opt. Lett.* **35**, 3994 (2010).
53. O. Raz, O. Pedatzur, B. D. Bruner, and N. Dudovich, "Spectral caustics in attosecond science," *Nat. Photonics* **6**, 170 (2012).
54. J. A. Pérez-Hernández, M. F. Ciappina, M. Lewenstein, L. Roso, and A. Zair, "Beyond carbon *k*-edge harmonic emission using a spatial and temporal synthesized laser field," *Phys. Rev. Lett.* **110**, 053001 (2013).
55. P. Wei, J. Miao, Z. Zeng, C. Li, X. Ge, R. Li, and Z. Xu, "Selective enhancement of a single harmonic emission in a driving laser field with subcycle waveform control," *Phys. Rev. Lett.* **110**, 233903 (2013).
56. F. Brizuela, C. M. Heyl, P. Rudawski, D. Kroon, L. Rading, J. M. Dahlström, J. Mauritsson, P. Johnsson, C. L. Arnold, and A. L'Huillier, "Efficient high-order harmonic generation boosted by below-threshold harmonics," *Sci. Rep.* **3**, 1410 (2013).

57. P. Wei, Z. Zeng, J. Jiang, J. Miao, Y. Zheng, X. Ge, C. Li, and R. Li, "Selective generation of an intense single harmonic from a long gas cell with loosely focusing optics based on a three-color laser field," *Appl. Phys. Lett.* **104**, 151101 (2014).
58. C. Jin, G. Wang, H. Wei, A.-T. Le, and C. D. Lin, "Waveforms for optimal sub-keV high-order harmonics with synthesized two- or three-colour laser fields," *Nat Commun* **5**, 4003 (2014).
59. S. Haessler, T. Balčiūnas, G. Fan, G. Andriukaitis, A. Pugžlys, A. Baltuška, T. Witting, R. Squibb, A. Zaïr, J. W. G. Tisch, J. P. Marangos, and L. E. Chipperfield, "Optimization of quantum trajectories driven by strong-field waveforms," *Phys. Rev. X* **4**, 021028 (2014).
60. T. Kroh, C. Jin, P. Krogen, P. D. Keathley, A.-L. Calendron, J. P. Siqueira, H. Liang, E. L. Falcão-Filho, C. D. Lin, F. X. Kärtner, and K.-H. Hong, "Enhanced high-harmonic generation up to the soft x-ray region driven by mid-infrared pulses mixed with their third harmonic," *Opt. Express* **26**, 16955 (2018).
61. M. Sayrac, A. A. Kolomenskii, J. Dong, and H. A. Schuessler, "Generation of enhanced even harmonics of fundamental radiation in temporally separated two-color laser fields," *J. Electron Spectrosc. Relat. Phenom.* **233**, 22 (2019).
62. S. Mitra, S. Biswas, J. Schötz, E. Pisanty, B. Förg, G. A. Kavuri, C. Burger, W. Okell, M. Högner, I. Pupeza, V. Pervak, M. Lewenstein, P. Wnuk, and M. F. Kling, "Suppression of individual peaks in two-colour high harmonic generation," *J. Phys. B: At. Mol. Opt. Phys.* **53**, 134004 (2020).
63. A. Zaïr, M. Holler, A. Guandalini, F. Schapper, J. Biegert, L. Gallmann, U. Keller, A. S. Wyatt, A. Monmayrant, I. A. Walmsley, E. Cormier, T. Augustine, J. P. Caumes, and P. Salières, "Quantum path interferences in high-order harmonic generation," *Phys. Rev. Lett.* **100**, 143902 (2008).
64. S. R. Abbing, F. Campi, F. S. Sajjadian, N. Lin, P. Smorenburg, and P. M. Kraus, "Divergence control of high-harmonic generation," *Phys. Rev. Appl.* **13**, 054029 (2020).
65. X. Ren, V. Makhija, A.-T. Le, J. Troß, S. Mondal, C. Jin, V. Kumarappan, and C. Trallero-Herrero, "Measuring the angle-dependent photoionization cross section of nitrogen using high-harmonic generation," *Phys. Rev. A* **88**, 043421 (2013).
66. B. Langdon, J. Garlick, X. Ren, D. J. Wilson, A. M. Summers, S. Zigo, M. F. Kling, S. Lei, C. G. Elles, E. Wells, E. D. Poliakoff, K. D. Carnes, V. Kumarappan, I. Ben-Itzhak, and C. A. Trallero-Herrero, "Carrier-envelope-phase stabilized terawatt class laser at 1 kHz with a wavelength tunable option," *Opt. Express* **23**, 4563 (2015).
67. C. Burger, W. F. Frisch, T. M. Kardaś, M. Trubetskov, V. Pervak, R. Moshhammer, B. Bergues, M. F. Kling, and P. Wnuk, "Compact and flexible harmonic generator and three-color synthesizer for femtosecond coherent control and time-resolved studies," *Opt. Express* **25**, 31130 (2017).
68. T. Kita, T. Harada, N. Nakano, and H. Kuroda, "Mechanically ruled aberration-corrected concave gratings for a flat-field grazing-incidence spectrograph," *Appl. Opt.* **22**, 512 (1983).
69. A. Kramida, Yu. Ralchenko, J. Reader, and NIST ASD Team, NIST Atomic Spectra Database (ver. 5.8), [Online]. Available: <https://physics.nist.gov/asd> [2021, February 8]. National Institute of Standards and Technology, Gaithersburg, MD. (2020).
70. W.-H. Xiong, L.-Y. Peng, and Q. Gong, "Recent progress of below-threshold harmonic generation," *J. Phys. B: At. Mol. Opt. Phys.* **50**, 032001 (2017).
71. N. Ishii, A. Kosuge, T. Hayashi, T. Kanai, J. Itatani, S. Adachi, and S. Watanabe, "Quantum path selection in high-harmonic generation by a phase-locked two-color field," *Opt. Express* **16**, 20876 (2008).
72. M. B. Gaarde, J. L. Tate, and K. J. Schafer, "Macroscopic aspects of attosecond pulse generation," *J. Phys. B: At. Mol. Opt. Phys.* **41**, 132001 (2008).
73. C. Trallero-Herrero, C. Jin, B. E. Schmidt, A. D. Shiner, J.-C. Kieffer, P. B. Corkum, D. M. Villeneuve, C. D. Lin, F. Légaré, and A. T. Le, "Generation of broad XUV continuous high harmonic spectra and isolated attosecond pulses with intense mid-infrared lasers," *J. Phys. B: At. Mol. Opt. Phys.* **45**, 011001 (2011).
74. A. D. Shiner, C. Trallero-Herrero, N. Kajumba, H.-C. Bandulet, D. Comtois, F. Légaré, M. Giguère, J.-C. Kieffer, P. B. Corkum, and D. M. Villeneuve, "Wavelength scaling of high harmonic generation efficiency," *Phys. Rev. Lett.* **103**, 073902 (2009).
75. A. Shiner, C. Trallero-Herrero, N. Kajumba, B. Schmidt, J. Bertrand, K. T. Kim, H.-C. Bandulet, D. Comtois, J.-C. Kieffer, D. Rayner, P. Corkum, F. Légaré, and D. Villeneuve, "High harmonic cutoff energy scaling and laser intensity measurement with a 1.8 m laser source," *J. Mod. Opt.* **60**, 1458 (2013).
76. P. B. Corkum, "Plasma perspective on strong field multiphoton ionization," *Phys. Rev. Lett.* **71**, 1994 (1993).
77. J. L. Krause, K. J. Schafer, and K. C. Kulander, "High-order harmonic generation from atoms and ions in the high intensity regime," *Phys. Rev. Lett.* **68**, 3535 (1992).
78. M. B. Gaarde, F. Salin, E. Constant, P. Balcou, K. J. Schafer, K. C. Kulander, and A. L'Huillier, "Spatiotemporal separation of high harmonic radiation into two quantum path components," *Phys. Rev. A* **59**, 1367 (1999).
79. F. Schapper, M. Holler, T. Auguste, A. Zaïr, M. Weger, P. Salières, L. Gallmann, and U. Keller, "Spatial fingerprint of quantum path interferences in high order harmonic generation," *Opt. Express* **18**, 2987 (2010).
80. X. He, J. M. Dahlström, R. Rakowski, C. M. Heyl, A. Persson, J. Mauritsson, and A. L'Huillier, "Interference effects in two-color high-order harmonic generation," *Phys. Rev. A* **82**, 033410 (2010).
81. H. Wikmark, C. Guo, J. Vogelsang, P. W. Smorenburg, H. Coudert-Alteirac, J. Lahl, J. Peschel, P. Rudawski, H. Dacasa, S. Carlström, S. Maclot, M. B. Gaarde, P. Johnsson, C. L. Arnold, and A. L'Huillier, "Spatiotemporal coupling of attosecond pulses," *Proc. Natl. Acad. Sci.* **116**, 4779 (2019).
82. L. Quintard, V. Strelkov, J. Vabek, O. Hort, A. Dubrouil, D. Descamps, F. Burgy, C. Péjot, E. Mével, F. Catoire, and E. Constant, "Optics-less focusing of XUV high-order harmonics," *Sci. Adv.* **5**, eaau7175 (2019).

Supplementary information: Enhancing high-order harmonic generation by controlling the diffusion of the electron wavepacket

T. SEVERT^{1, ‡}, J. TROSS^{1, ‡}, G. KOLLIPOULOS¹, I. BEN-ITZHAK^{1, *}, AND C. A. TRALLERO-HERRERO^{1,2, **}

¹J.R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA

²Department of Physics, University of Connecticut, Storrs, Connecticut 06269, USA

* Corresponding author: ibi@phys.ksu.edu

** Corresponding author: carlos.trallero@uconn.edu

‡ These authors contributed equally to this work.

Compiled June 8, 2021

© 2021 Optical Society of America

<http://dx.doi.org/10.1364/ao.XX.XXXXXX>

1. EXPERIMENTAL METHOD

This section describes the experimental methods used in our paper, which studies the enhancement of high-order harmonic generation driven by bichromatic 800 – 266-nm laser fields. Fig. 1(a) in that paper shows a schematic of the experimental setup.

In this experiment, we use a Ti:Sapphire laser with a 27-fs pulse duration, full-width-half-maximum in intensity, and a maximum pulse energy of 20 mJ at a 1-kHz repetition rate [1]. We limit the intensity in the high harmonic generation medium by placing beamsplitters before the experimental apparatus. Additionally, to variably control the attenuation level of the input pulse energy before the interferometer, we reflect the 800-nm laser pulses through a set of germanium plates at Brewster's angle for 800 nm, providing a maximum pulse energy of 2 mJ. This input pulse energy is kept constant for all measurements presented in this paper.

To generate the $\omega - 3\omega$ laser field, we introduce a two-color interferometer immediately following the germanium plates, as shown in Fig. 1(a) of the paper. To avoid depletion effects in the fundamental driving field, the third harmonic is generated in one arm of the interferometer instead of before it. The benefit of this approach is that it leads to a better wavefront of the 800-nm field and therefore significantly improves the spatial quality of the generated harmonic beam.

Once entering the interferometer, the 800-nm beam is split in two using a beamsplitter. To control the relative intensities between the fundamental and the third harmonic, beamsplitters with different reflection/transmission ratios are used. The 800-nm beam transmitted through the beamsplitter propagates through the delay arm of the interferometer, noted as "Arm A" in Fig. 1(a) of the paper. The beam transmits through a $\lambda/2$ waveplate, which we use to rotate the polarization by 90° when tuning the delay between the arms to find temporal overlap between the 266-nm and 800-nm laser pulses using difference frequency generation. When generating harmonics using $\omega - 3\omega$ beam, the waveplate is tuned to maintain the initial polarization of the 800-nm pulse. We leave the waveplate inside the interferometer because removing it changes the dispersion of the pulse as well as its time-delay with respect to the other arm. Then, the 800-nm light reflects off a retroreflector on a piezo driven linear stage, which controls the relative time-delay/phase between the fields. Finally, the beam transmits through a dichroic beamsplitter, reflects off several steering mirrors, and enters the vacuum chamber through a 1-mm thick UVFS entrance window where the harmonics are produced and measured. Note that the dispersion of the 800-nm beam is minimized, by adjusting the compressor grating, to produce the largest cutoff photon energy, the brightest harmonics, and the highest ionization yield, simultaneously, at a fixed focal position. Then to determine the global conditions for the single- and two-color driving fields, we adjust the focus of the beams with respect to the gas jet to maximize the yield of the plateau harmonics.

Meanwhile, in the other arm of the interferometer, labeled as "Arm B" in Fig. 1(a) of the manuscript, the 800-nm beam reflects off the first beamsplitter and transmits through a 2-mm thick window of SF11 glass, a second harmonic generation BBO (SHG-BBO), calcite for controlling the delay between the pulses, a $\lambda/2$ zero-order waveplate to rotate the polarization of the 800-nm light, and a third harmonic generation BBO (THG BBO). We use the SF11 glass to compensate for the negative GVD and to maximize the third harmonic generation efficiency (approximately 15%). The third-harmonic then reflects off 4 dichroic beamsplitters to remove the

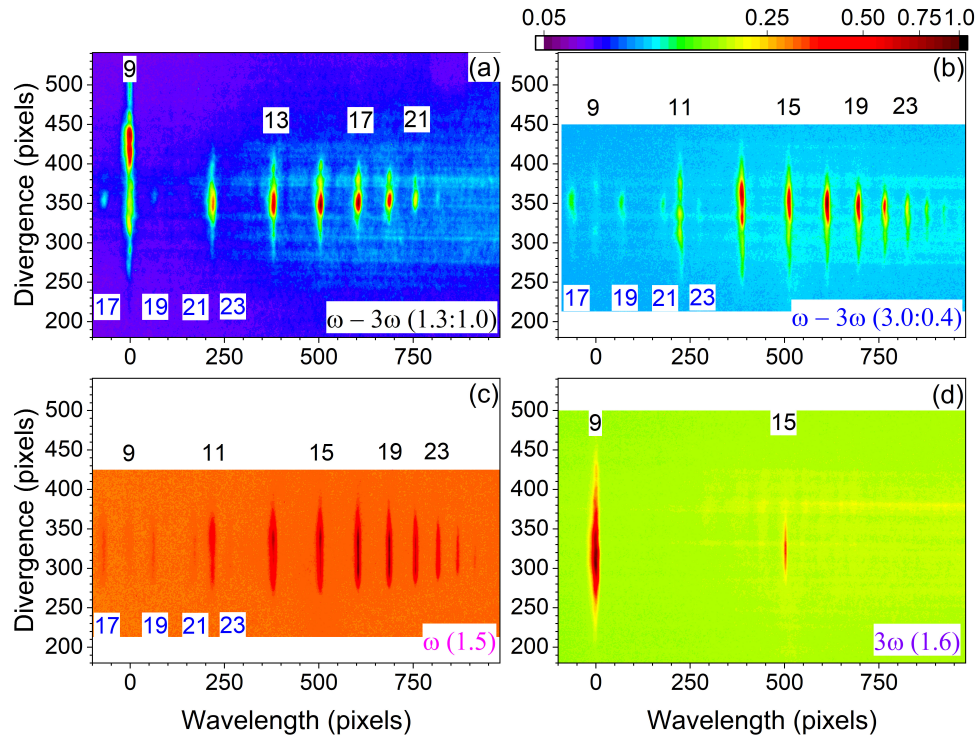


Fig. 1. The raw camera images of the harmonics for the two-color fields with (a) (1.3:1.0) and (b) (3.0:0.4) intensities ratios as well as the maximized single color (c) 800 nm and (d) 266 nm results. Note that the x and y axes of the plot are scaled linearly in units of pixels while the z axis, i.e. color scale, is logarithmic. Furthermore, the color axis is scaled such that the maximum value in each image is set to unity, meaning all plots are shown over the same dynamics range. In addition, the black numbers on the top of each individual figure represent the harmonic labelings for the first order diffraction while the lower blue numbers represent the second order diffraction.

residual unconverted 800- and 400-nm light. After the final beamsplitter, the third harmonic is spatially and temporally recombined with the 800-nm beam that propagates through “Arm A.” To spatially overlap the beams, we image both foci using a CCD camera that is sensitive to both wavelengths. To ensure the beams are as collinear as possible near the focus, we align the beams such that they are spatially overlapped at two camera positions about 2.5 cm apart. The error in the collinearity of the beams is on the order of a few mrad. It is important to note that the beams are not perfectly collinear since we see minor phase-dependent spatial asymmetries in the harmonic divergence angle.

We characterize the laser pulses after the interferometer using a home-built self-diffraction FROG [2], thus accounting for the dispersion caused by propagating through the interferometer, in air, and by transmission through the entrance window into the vacuum chamber. Note that during the FROG measurements, a 1-mm thick window of UVFS is inserted into the laser beam’s path to account for the dispersion in the entrance window into the vacuum chamber. As a result, the laser pulses’ characterization is performed such that we measure the pulse duration in the HHG generation medium to the best of our ability. At this point, the fundamental field is measured to have a pulse duration of 27 fs, which is the shortest we could compress the pulse at the exit of the laser system. On the other hand, the third harmonic has a pulse duration of approximately 59 fs, which is slightly positively chirped from a Fourier-transform-limited pulse duration of 53 fs.

To determine the peak intensity in the gas jet, we image the focus of each color separately using a CCD camera, measure their pulse energies after transmission through an equivalent 1-mm thick UVFS glass window, and use the intensity envelope retrieved from the FROG traces. For reference, Table 1 includes the beam radii in the gas jet for the different experimental conditions. For the approximately equal intensity ratio of (1.3:1.0), for which the intensity of the 800-nm field is 1.3×10^{14} W/cm² and the 266-nm field is 1.0×10^{14} W/cm², the pulse energies of the 800- and 266-nm fields at the exit of the interferometer are 327 and 248 μ J, respectively. For the unequal intensity ratio of (3.0:0.4), the pulse energies of the 800- and 266-nm fields at the exit of the interferometer are 800 and 90 μ J, respectively. The laser powers for all the experimental conditions are repeated in Table 1.

Finally, the two-color beam propagates into the vacuum chamber, where the light is focused onto an argon gas jet, introduced through a glass capillary with an inner diameter of 250 μ m. Note, the backing pressure of the argon gas jet was held constant at approximately 1100 Torr throughout all our measurements. The foci of the single- and two-color beams are always located before the gas jet. The specific distance between the foci and the gas jet are listed in Table 1. The produced harmonics then propagate through a differentially pumped region into a spectrometer, with an entrance slit of 450 μ m located approximately 38 cm from the gas jet. The harmonics then diffract off a concave VUV grating and are dispersed onto an MCP-phosphor detector. Next, a camera images the resulting fluorescence from the phosphor screen. To determine the yield of each harmonic, we integrate the fluorescence captured by the camera for 2 seconds. Several raw sample images are shown in Fig. 1, here in the supplementary information, for the various

Table 1. This table contains information about the distance of the focus from the jet (all foci are located before the jet), the radius of the beams ($1/e^2$ in intensity) in the gas jet, and the laser pulse energy after accounting for the entrance window into the vacuum chamber.

Laser fields	Focus distance from jet	ω beam radius	3ω beam radius	ω pulse energy	3ω pulse energy
$\omega - 3\omega$ (1.3:1.0)	4 mm	$50.0 \pm 3.5 \mu\text{m}$	$33.9 \pm 2.5 \mu\text{m}$	327 μJ	248 μJ
$\omega - 3\omega$ (3.0:0.4)	4 mm	$50.0 \pm 3.5 \mu\text{m}$	$33.9 \pm 2.5 \mu\text{m}$	800 μJ	90 μJ
ω (1.5)	10 mm	$119 \pm 6.5 \mu\text{m}$	—	2000 μJ	—
3ω (1.6)	5 mm	—	$43.0 \pm 3.5 \mu\text{m}$	—	310 μJ

experimental conditions. For all the data shown in the manuscript, we corrected for the polarization-sensitive efficiency of the grating, the wavelength-dependent detection efficiency of the micro-channel plates [3], and the nonuniform angular acceptance due to the spectrometer's entrance slit.

When generating harmonics using the "optimized" 800-nm laser field, we remove the interferometer from the beam path, allowing the full 2 mJ pulses to focus into the gas jet. To reduce the intensity in the target medium, the focus is moved further away from the gas jet to maximize the harmonic yield. The peak intensity of the single-color 800-nm field producing the maximum harmonic yield is $1.5 \times 10^{14} \text{ W/cm}^2$. We use a similar approach for the "optimized" 266-nm field, with the exception that we need the set of third-harmonic generation optics and filters shown in Arm B of the interferometer. The resulting 266-nm pulse energy is 310 μJ in this case.

Finally, the most important characteristic of our experimental setup is the high stability of the interferometer. To perform the two-color measurements, the stability between the laser beams propagating along the two arms of the interferometer need to be much less than 0.9 fs, which is the period of the 266-nm field. To achieve this stability, we vibrationally isolate the interferometer from the optics table using mechanical vibration isolation mounts (Newport VIB100). We measure the stability by propagating a frequency doubled continuous wave ND:YAG-laser beam (with wavelength of 532 nm) through the interferometer and image the spatial interference approximately 5 cm behind the recombination mirror. Fig. 1(b) in the manuscript shows the projection of the measured spatial interference fringes as a function of time. By extracting the phase of the image as shown in Fig. 1(c) of the paper using Fourier analysis, we measure a timing jitter between the arms to have a root-mean-square error (RMSE) of 50 as over 170 seconds, which is significantly smaller than the 0.9 fs period of the 266-nm laser pulse.

2. DISCUSSION OF THE LEWENSTEIN MODEL

To interpret the observed phase shifts presented in Fig. 3(d) of the paper, we must first understand what physical mechanisms affect the HHG yield at the single-atom level. It is known that the resulting harmonic spectrum $S(\omega)$ is proportional to the absolute square of the Fourier transform of the time-dependent induced dipole [4–6], i.e. $S(\omega) \propto |\mathcal{F}[D(t)]|^2$. Within the quantum mechanical strong-field approximation (SFA), i.e. the Lewenstein model [7], the time-dependent induced dipole, assuming the saddle-point approximation and a linearly-polarized driving field, is given by:

$$D(t) = -i \int_{-\infty}^t dt' \left(\frac{-2\pi i}{t - t' - i\epsilon} \right)^{3/2} d^*[p_s + A(t)] d[p_s + A(t')] E(t') e^{-iS(p_s, t, t')} + c.c. \quad (1)$$

in atomic units, following the notation in Ref. [6]. The ϵ is a small positive regularization constant used to smooth the irregularity, p_s represents the saddle-point approximation solution of the canonical momentum, $E(t')$ is the instantaneous electric field at time t' , $S(p_s, t, t')$ is the quasiclassical action of the electron, and $d[p_s + A(t')]$ represents the dipole matrix element for electrons with momenta $p_s + A(t')$.

To determine how bichromatic fields alter $D(t)$ and hence the observed HHG spectrum $S(\omega)$, we describe the various terms in Eq. 1. Specifically, the $d[p_s + A(t')] E(t')$ term describes the ionization of the target at time t' , which some have replaced with the more accurate ADK or PPT ionization rates, e.g. see the textbook in Ref. [5]. The $d^*[p_s + A(t)]$ term represents the recombination of the electron with the remaining core at time t . It is important to note that this term only depends on the return momentum of the electron, i.e. $p_s + A(t)$, and therefore cannot be controlled by the bichromatic field for a specific harmonic order, assuming the ground state is not depleted by ionization. Finally, the $(t - t')^{-3/2}$ term represents the quantum diffusion of the returning electron wavepacket, which depends on the excursion time of the electron in the continuum, i.e. $t - t'$. Therefore, to summarize, the bichromatic field mainly influences the HHG yield by changing the ionization rate and the quantum diffusion, i.e. excursion time, of the relevant electron trajectories.

3. TRAJECTORY CALCULATIONS

We calculate the classical electron trajectories in a two-color driving field using the standard approach [5]. Note that the electric field due to the Coulomb attraction between the electron and remaining ion is neglected because we assume that the electric field of the laser is much larger than this attraction. Furthermore, all equations included in this section are given in atomic units. Briefly, we write the electric field as

$$E(t) = E_0 [\cos(\omega_0 t) + \alpha \cos(n\omega_0 t + \phi)], \quad (2)$$

where E_0 is the amplitude of the electric field of the fundamental laser field with angular frequency ω_0 , n is the harmonic order that is mixed with the fundamental field, α is the ratio of the n th harmonic and fundamental electric fields, and ϕ is the relative phase between these two fields.

Assuming linear polarization and that the electron is released at an ionization time t' at rest ($\dot{x} = 0$) and from the ion core (located at $x = 0$), we calculate the scaled position of the electron trajectory at time t to be

$$\frac{x}{E_0/\omega_0^2} = \cos(\omega_0 t) - \cos(\omega_0 t') + \omega_0(t - t') \sin(\omega_0 t') + \frac{\alpha}{n^2} \{ \cos(n\omega_0 t + \phi) - \cos(n\omega_0 t' + \phi) + n\omega_0(t - t') \sin(n\omega_0 t' + \phi) \}. \quad (3)$$

Then, we numerically solve for the electron's return time back to the core, t_R , by setting $x = 0$ and requiring $t_R > t'$. All returning electron trajectories within one optical cycle of the fundamental field are solved for, including for the rare cases when trajectories return multiple times.

Then, the kinetic energy of the returning electron is

$$KE = 2U_p \left[\sin(\omega_0 t_R) - \sin(\omega_0 t') + \frac{\alpha}{n} \{ \sin(n\omega_0 t_R + \phi) - \sin(n\omega_0 t' + \phi) \} \right]^2, \quad (4)$$

where U_p is the pondermotive energy of a free electron within the single-color laser field with angular frequency ω_0 , explicitly given by:

$$U_p = \frac{E_0^2}{4\omega_0^2}. \quad (5)$$

Finally, the photon energy E_γ is:

$$E_\gamma = KE + I_p, \quad (6)$$

where I_p is the ionization potential of the target.

It is important to note that by solving for the electron trajectories assuming a continuous wave electric field, as written in Eq. 2, we are neglecting the influence of the envelope of the laser pulse. However, given that our laser pulses are long (> 10 cycles for the 800-nm field), the electric-field strength does not change significantly from cycle to cycle, thereby minimizing the effect of the envelope. Furthermore, the HHG spectrum is dominated by the peak of the envelope since that is where the intensity, and thus ionization rate, is highest. Finally, it is also important to note that even if the peak electric field strength E_0 changes, as long as the intensity ratio (α) between the colors stays approximately the same, the electron trajectories also remain the same except for a change in the returning kinetic energy through the alteration of the pondermotive energy. Therefore, electron trajectories corresponding to higher photon energies at the peak intensity shift to slightly lower photon energies at lower intensities on either the rising or falling edges of the pulse. Furthermore, it is important to note that these calculations are not state of the art and are used as an interpretation tool of our experimental findings. A non-exhaustive list of more precise models for HHG are quantitative rescattering theory [6, 8], those based on the principle of detailed balancing [9, 10], and improved SFA [11].

In the paper, we make the statement that the results demonstrating control over the excursion times of the trajectories are independent of the wavelength of the fundamental driving field. This can be seen by solving Equations 3 and 4 in terms of the dimensionless parameters $\omega_0 t$ and $\omega_0 t'$. The only thing that changes is the mapping of the trajectories to energy due to the pondermotive energy (U_p) of the electron. Furthermore, switching targets also modifies how the trajectories map to photon energy in HHG via the ionization potential, I_p , shown in Equation 6.

REFERENCES

1. B. Langdon, J. Garlick, X. Ren, D. J. Wilson, A. M. Summers, S. Zigo, M. F. Kling, S. Lei, C. G. Elles, E. Wells, E. D. Poliakoff, K. D. Carnes, V. Kumarappan, I. Ben-Itzhak, and C. A. Trallero-Herrero, "Carrier-envelope-phase stabilized terawatt class laser at 1 kHz with a wavelength tunable option," *Opt. Express* **23**, 4563 (2015).
2. R. Trebino, K. W. DeLong, D. N. Fittinghoff, J. N. Sweetser, M. A. Krumbügel, B. A. Richman, and D. J. Kane, "Measuring ultrashort laser pulses in the time-frequency domain using frequency-resolved optical gating," *Rev. Sci. Instruments* **68**, 3277 (1997).
3. C. Martin and S. Bowyer, "Quantum efficiency of opaque CsI photocathodes with channel electron multiplier arrays in the extreme and far ultraviolet," *Appl. Opt.* **21**, 4206 (1982).
4. C. J. Joachain, N. J. Kylstra, and R. M. Potvliege, *Atoms in Intense Laser Fields* (Cambridge University Press, 2009).
5. Z. Chang, *Fundamentals of Attosecond Optics* (CRC Press, 2011).
6. C. D. Lin, A.-T. Le, C. Jin, and H. Wei, *Attosecond and Strong-Field Physics* (Cambridge University Press, 2018).
7. M. Lewenstein, P. Balcou, M. Y. Ivanov, A. L'Huillier, and P. B. Corkum, "Theory of high-harmonic generation by low-frequency laser fields," *Phys. Rev. A* **49**, 2117 (1994).
8. C. D. Lin, A.-T. Le, C. Jin, and H. Wei, "Elements of the quantitative rescattering theory," *J. Phys. B: At. Mol. Opt. Phys.* **51**, 104001 (2018).
9. M. V. Frolov, N. L. Manakov, A. A. Silaev, N. V. Vvedenskii, and A. F. Starace, "High-order harmonic generation by atoms in a few-cycle laser pulse: Carrier-envelope phase and many-electron effects," *Phys. Rev. A* **83**, 021405(R) (2011).
10. M. V. Frolov, N. L. Manakov, A. M. Popov, O. V. Tikhonova, E. A. Volkova, A. A. Silaev, N. V. Vvedenskii, and A. F. Starace, "Analytic theory of high-order-harmonic generation by an intense few-cycle laser pulse," *Phys. Rev. A* **85**, 033416 (2012).
11. D. B. Milošević and W. Becker, "Improved strong-field approximation and quantum-orbit theory: Application to ionization by a bicircular laser field," *Phys. Rev. A* **93**, 063418 (2016).

6.4 Enhancing HHG in $\omega - 2\omega$ and $\omega - 3\omega$ fields

In this section, we present a draft of a manuscript, which is a follow up to the submitted paper in Section 6.3. In this paper, we focus on comparing the enhancement of HHG driven by bichromatic $\omega - 2\omega$ (800 – 400-nm) and $\omega - 3\omega$ (800 – 266-nm) driving fields with their single-color 800-, 400-, and 266-nm counterparts. When making this comparison, we take the same approach as in the previous section. Specifically, we take into account that a laser system can only provide finite amounts of pulse energy, so we fix the total energy input into our system to 2 mJ. We observe that all bichromatic fields outperform the fundamental 800-nm driving field for the common photon energies, usually by one order of magnitude or more. Furthermore, we show that the single-color 400- and 266-nm driving fields typically provide similar photon flux as the two-color drivers at common photon energies. This result suggests that if experimentalists are only interested in energies that these single-color driving-fields generate, they are better off using them than the bichromatic fields because the optics setup to generate the single-color fields is relatively simpler to implement. Finally, we compare the divergences of the bichromatic and single-color driving fields. Generally, the $\omega - 3\omega$ fields outperform their counterparts, perhaps suggesting that they significantly enhance the contributions of the short electron trajectories.

To our knowledge, this paper provides the first comparison of HHG sources driven by $\omega - 2\omega$ and $\omega - 3\omega$ laser fields. With the next generation of high repetition rate but only a few mJ of pulse energy lasers becoming more widely available, techniques for boosting the harmonic beams' efficiency become more important. By comparing the $\omega - 2\omega$ and $\omega - 3\omega$ driving fields, we provide researchers with information for developing and improving their HHG based light sources.

In this project, Jan and I played similar roles as in the previous section. Specifically, Jan worked on the analysis to determine the enhancements while I analyzed the divergences. I prepared the the draft and figures of the manuscript with feedback from all coauthors.

Enhancing high-order harmonic generation in two-color laser fields: A comparison of single- and two-color schemes

JAN TROSS,^{1,‡} TRAVIS SEVERT,^{1,‡} GEORGIOS KOLLIPOPOULOS,¹
PRATAP TIMILSINA,¹ ITZIK BEN-ITZHAK,^{1,†} AND CARLOS A.
TRALLERO-HERRERO^{1,2,*}

¹*J.R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA*

²*Department of Physics, University of Connecticut, Storrs, Connecticut 06269, USA*

[‡] *These authors contributed equally to this work.*

* carlos.trallero@uconn.edu

† ibi@phys.ksu.edu

Abstract: We compare the enhancement of high-order harmonic generation in argon using 800–400- and 800–266-nm laser fields with their optimized single-color counterparts. We observe that the two-color fields generally outperform the single-color 800-nm field by factors of 2 to 3800, depending on the photon energy and generation scheme. From this comparison, we determine which scheme is optimal for each photon energy. We also observe that the divergence of HHG produced by the 800–266-nm laser fields is smaller than the other single and two-color driving fields, perhaps suggesting that the 800–266-nm fields optimize the recombination probability of the so called “short” electron trajectories.

© 2021 Optical Society of America under the terms of the [OSA Open Access Publishing Agreement](#)

1. Introduction

High-order harmonic generation (HHG) is an important technique, allowing researchers to produce vacuum-ultraviolet to soft X-Ray laser pulses using table-top setups. Although large synchrotrons and free-electron laser (FEL) facilities provide higher pulse energies than conventional HHG based laser sources, the laser pulses generated via HHG are capable of producing attosecond pulses with excellent spatial and temporal coherence properties [1–5], which only state-of-the-art FEL facilities are beginning to approach [6–8]. To make HHG based laser sources promising tools for a variety of fields of study, research must be devoted to increasing the overall photon flux to decrease data acquisition times and improve signal-to-noise ratios.

Since HHG typically has low conversion efficiencies on the order of 10^{-5} or lower [9, 10], researchers have studied a variety of methods for increasing the photon flux. Some researchers use a brute force approach, where they develop high power driving lasers to increase the photon flux and/or harmonic pulse energy on target [11–14]. Alternatively, others try to increase the efficiency of HHG by improving phase matching conditions, for example by using loose focusing geometries in conjunction with gas cells [15–18] or gas filled waveguides [19–22]. Further approaches explore changing the frequency of the driving field to increase the overall efficiency of HHG, for example using shorter wavelength [23–27] or multi-color driving fields [28–45]. In this paper, we focus on increasing the overall efficiency of the generated harmonics using two-color $\omega - 2\omega$ and $\omega - 3\omega$ driving laser fields.

Increasing the efficiency or flux of high harmonic generation using two-color $\omega - 2\omega$ laser fields has already been studied extensively in the past [29–36, 45], while using $\omega - 3\omega$ has only recently begun to be explored in detail [40, 41, 43, 44]. For example, Kim *et al.* [31] showed that high-order harmonics produced by orthogonally polarized 800–400-nm laser fields were more

than two orders of magnitude stronger than from the fundamental driving field alone, reporting a conversion efficiency as high as 5×10^{-5} for the 38th harmonic at 21.6 nm. Later, using the same approach, Kim *et al.* [33] increased the efficiency of the 38th harmonic by extending the length of their gas jet to 6 mm, reaching pulse energies of $0.6 \mu\text{J}$ with a conversion efficiency as high as 2×10^{-4} . More recently, Jin *et al.* [40, 41] theoretically showed that the efficiency of high-order harmonic generation can be improved by two or more orders of magnitude using an $\omega - 3\omega$ driving field. Their argument is that in the two-color $\omega - 3\omega$ fields, the relative phase between the fields is tuned to optimize the recombination probability of the “short trajectory” electrons. Following their theoretical predictions, Kroh *et al.* [44] systematically studied the enhancement of HHG driven by 2100-(ω) and 700-nm (3ω) driving fields, where they observed efficiency enhancements of 8.2 times in photon flux integrated from 20-70 eV and up to 2.2 times from 85-205 eV over the single-color 2100 nm laser field.

Hoping to take advantage of the wavelength scaling of the HHG efficiency using ultraviolet driving fields [23–27, 46], we study HHG driven by two-color 800–400-nm ($\omega - 2\omega$) and 800–266-nm ($\omega - 3\omega$) laser fields to improve the HHG efficiency from 15 to 40 eV when compared to the single-color 800-nm driving field. Additionally, we compare the relative HHG efficiency of the two-color driving fields with the same photon energies produced by the single-color 400- and 266-nm fields to determine whether it is worthwhile to use the more demanding two-color setup to generate certain photon energies.

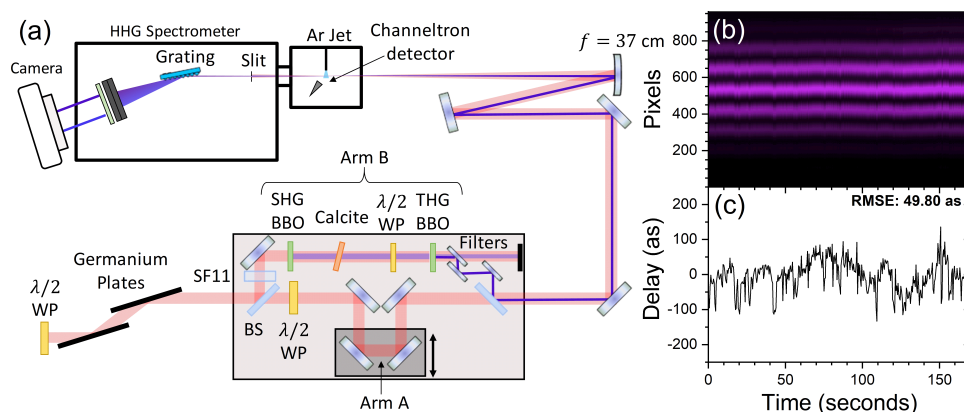
It is worth noting that we take a pragmatic experimentalist approach for comparing the relative efficiencies between the optimized single- and two-color driving fields. Since laser systems are typically limited in their maximum output power, we chose to fix the maximum power input into our experimental setup instead of, for example, the total pulse energies or peak intensities in the target medium. Therefore, due to the efficiency to generate the second and third harmonics of the fundamental 800-nm driving field, the two-color as well as single color 400- and 266-nm driving fields do not provide as much power on target as the fundamental driving field. Furthermore, we change phase-matching conditions, though admittedly in a limited range, for the different driving fields so we can compare the efficiency for the optimized conditions of each of our measurements. Even though the optimized two-color and single-color 400- and 266-nm fields have lower input power, they generally outperform the 800-nm driving pulse.

2. Experimental setup and methods

The goal of this experiment is to compare harmonics produced from two-color 800–400- and 800–266-nm laser fields to their optimized single-color counterparts. In this section, we briefly describe how we generate and measure the flux of the harmonics in the optimized single-color and two-color laser fields.

We begin with a Ti:Sapphire laser with a 27-fs pulse duration, full-width-half-maximum in intensity, and a maximum pulse energy of 20 mJ at a 1-kHz repetition rate [47]. Since we are using an in vacuum $f = 37.5$ -cm spherical mirror to focus the laser into the gas jet, we attenuate the pulse energy using beamsplitters before our experimental apparatus to limit the peak intensity in our target. To have variable attenuation of our input power, we reflect the 800-nm laser pulses through a set of Germanium plates at Brewster’s angle for 800 nm, providing a maximum pulse energy of 2 mJ before our experimental setup.

When generating harmonics using the optimized 800-nm laser field, we directly focus the laser pulse in an argon gas jet, introduced through a glass capillary with an inner diameter of $250 \mu\text{m}$. The backing pressure of the argon gas jet was held constant at approximately 1100 Torr throughout the measurements, raising the pressure in the vacuum chamber from 1×10^{-8} to 1×10^{-5} Torr. To change the phase-matching conditions, we scan the gas jet ± 2.5 cm throughout the focal profile while monitoring the relative ionization rate in the medium using a channeltron detector.



The produced harmonics then propagate through a differentially pumped region into a spectrometer, with an entrance slit of $450\text{ }\mu\text{m}$. The harmonics, then, diffract off a flat-field VUV grating and are dispersed onto an MCP-phosphor detector. Next, a camera collects the resulting fluorescence off the phosphor screen. To determine the yield of each harmonic, we integrate the fluorescence captured by the camera for 2 seconds. We also correct the images for the polarization sensitive efficiency of the grating, the wavelength-dependent detection efficiency of the micro-channel plates [48], and the nonuniform angular acceptance due to the spectrometer's entrance slit.

To produce the 266-nm laser field, we send the orthogonally polarized 800- and 400-nm fields directly after the SHG-BBO through a 0.25-mm thick piece of calcite, compensating for the delay between the 800- and 400-nm pulses. Then, the two-color beam passes through a zero-order $\lambda/2$ waveplate, which rotates the 800-nm light to the same polarization as the 400-nm light. The beam then propagates through a type-I BBO crystal (THG-BBO) that is 0.1-mm thick with an optimized cut angle for sum-frequency generation between the 800- and 400-nm pulses. Note that the resulting 266-nm field has the same polarization as the 800-nm field before the initial SHG-BBO. We finally separate the third harmonic from the fundamental and second harmonic using reflective dichroic beamsplitters. After filtering, the third harmonic conversion efficiency is 12% of the fundamental, leading to a maximum pulse energy of 310 μJ . The pulse duration of the 266-nm light was measured to be 59 fs, positively chirped.

To generate the $\omega - 2\omega$ and $\omega - 3\omega$ laser fields, we introduce a two-color interferometer immediately following the germanium plates, as shown in Fig. 1(a). To avoid depletion effects in the fundamental driving field, we generate the second and third harmonics in one arm of the interferometer instead of before it, and therefore significantly improves the spatial quality of the beams produced by HHG. Explicitly, the 800-nm laser beam enters the interferometer and is split using a beamsplitter. To control the relative intensities between the fundamental and either second or third harmonics, we use beamsplitters with different reflection/transmission ratios.

The 800-nm beam transmitted through the beamsplitter propagates through the delay arm of the interferometer, noted as "Arm A" in Fig. 1(a). The beam transmits through a $\lambda/2$ waveplate, which only rotates the polarization of the light by 90° when studying the $\omega - 2\omega$ driving field. Since we do not need to rotate the polarization for the $\omega - 3\omega$ measurements, we tune the waveplate to maintain the initial polarization. Note, the waveplate remained in the interferometer to ensure the group-velocity-dispersion (GVD) of the 800-nm pulse is the same for the $\omega - 2\omega$ and $\omega - 3\omega$ measurements. Then, the 800-nm light reflects off a retroreflector on a piezo controlled linear stage which controls the relative time-delay/phase between the fields. Finally, the beam transmits through a dichroic beamsplitter, reflects off several steering mirrors, and enters the vacuum chamber where the harmonics are produced and measured. Note that the dispersion of the 800-nm beam is optimized to produce the largest cutoff photon energy, the brightest harmonics, and the highest ionization rate measured by the channeltron detector, simultaneously.

Meanwhile, in the other arm of the interferometer, labeled as "Arm B" in Fig. 1(a), the 800-nm beam reflects off the first beamsplitter and transmits through a 2-mm thick piece of SF11 glass and the SHG-BBO. We use the SF11 glass to compensate for the negative GVD such that the second harmonic is produced with the optimal conversion efficiency. To generate the third harmonic, we place the additional optics described above after the SHG-BBO, as shown in Fig. 1(a). The generated second or third harmonic then reflects off 4 dichroic beamsplitters. After the final beamsplitter, the second or third harmonic is spatially and temporally recombined with the 800-nm beam that propagated through "Arm A." Finally, the two-color beam propagates into the vacuum chamber, where the light is focused into the argon gas jet.

For our two-color measurements to be successful, we need to have a stability between the two arms that is "much" less than the period of the shortest wavelength driving field, which is 0.9 fs for the 266-nm field. To achieve this stability, we vibrationally isolated the interferometer from the optics table. We measure the stability by propagating a frequency doubled continuous wave ND:YAG laser through the interferometer and image the spatial interference at the exit. In Fig. 1(b), we show the measured spatial interference fringes as a function of time. By extracting the phase of the image using Fourier analysis, as shown in Fig. 1(c), we measure a timing jitter between the arms that has a root-mean-square error (RMSE) of 50 as over 170 seconds, which is significantly smaller than the period of the 266-nm laser pulse.

3. Optimized single-color driving fields

In this section, we compare the harmonics produced by the optimized single-color driving-fields. Due to the wavelength scaling of HHG efficiency for driving fields of 800-nm and shorter [26], we expect the HHG photon flux to significantly improve with shorter wavelength driving fields. Driving high-order harmonics using single-color laser fields may have some advantages over the two-color counterparts. Firstly, a single-color optical setup is significantly easier to design and build than a phase stabilized two-color setup, especially if one needs to use a two-color interferometer like discussed in the previous section. Secondly, the 400- and 266-nm driving fields improve the energy spacing between adjacent harmonics, making the harmonics easier to spatially separate, for example using a monochromator [50,51]. However, the main drawback of shorter wavelength driving fields is that the harmonic cutoff shifts to lower energies due to the reduction of the pondermotive energy of the electron [9, 10].

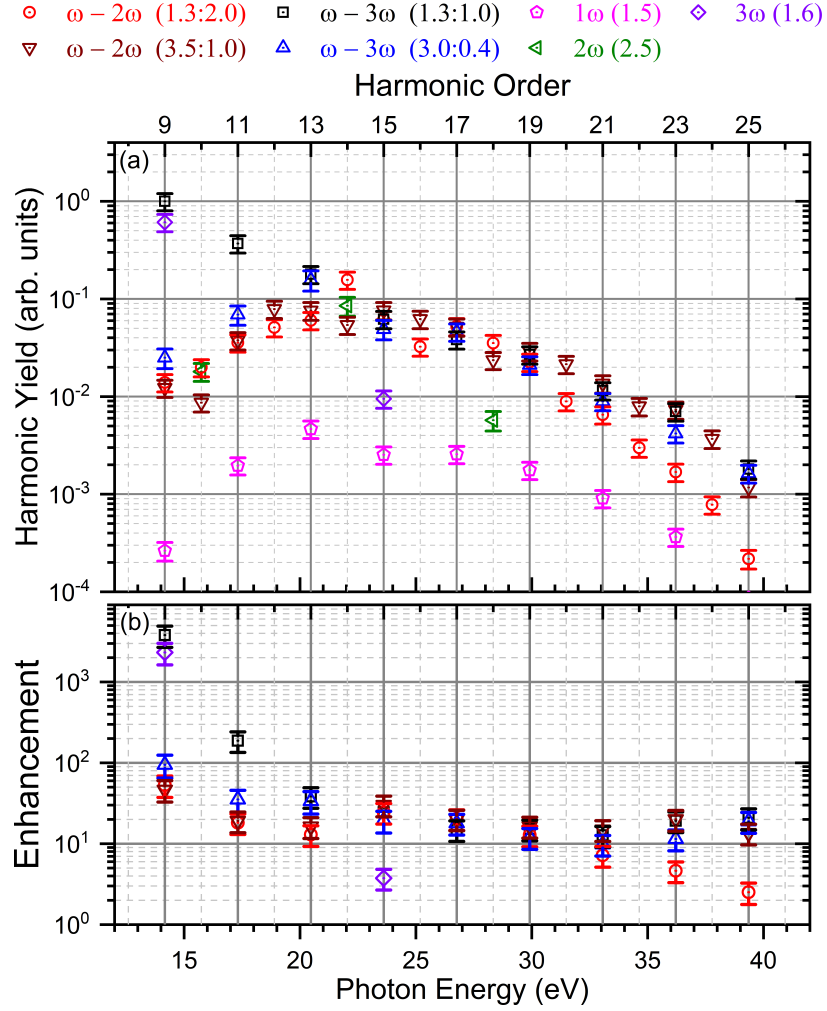


Fig. 2. (a) The integrated harmonic yields for the single color 800-nm (1ω), 400-nm (2ω), and 266-nm (3ω) fields as well as the two-color 800-400- ($\omega - 2\omega$) and 800-266-nm ($\omega - 3\omega$) fields. In the figure legend, the number in parenthesis represents the intensity, in units of 10^{14} W/cm². For the two-color fields, the first number represents the intensity of the fundamental field while the second number is the intensity of the second color. (b) The relative enhancement of the HHG yields over the single-color 800-nm field for similar photon energies.

In Fig. 2(a), we show the comparison between the optimized single color 800-, 400-, and 266-nm driving fields after correcting the detection efficiencies of each individual harmonic. To compare the different single-color fields, we optimize the position of the jet with respect to the focus, thereby changing the phase-matching conditions. In these optimized conditions, the peak intensities of the 800-, 400-, and 266-nm laser fields are 1.5×10^{14} , 2.5×10^{14} , and 1.6×10^{14} W/cm², respectively, with input pulse energies of 2 mJ, 880 μ J, and 310 μ J, respectively. To keep the intensities in the gas medium lower, the gas jet is moved significantly away from the laser's focus, giving the 800- and 400-nm driving fields larger interaction volumes than the 266-nm field.

Even though the 800-nm driving field has more input power, the single-color 400- and 266-nm pulses outperform the 800-nm driving field, as seen in Fig. 2(a). Comparing the common photon

energies produced by the 800- and 266-nm fields, we find that the photon energies of 14.4 and 24.0 eV are enhanced by factors of approximately 2300 and 4, respectively, when driving HHG with 266-nm as compared to the fundamental 800-nm field, as shown in Fig. 2(b). The decrease in yield in HHG driven with 266 nm at 24 eV is expected since this photon energy is beyond the expected cutoff for the 266-nm driving field using the standard estimate of the cutoff photon energy [9, 10].

4. Two-color driving fields

In this section, we focus on the results for two-color 800–400-nm and 800–266-nm driving fields. As has been previously shown [29–33, 52], mixing ω and 2ω laser fields breaks the inversion symmetry between half-cycles of the fundamental driving field, leading to the emission of both odd and even harmonics. To the contrary, the $\omega - 3\omega$ field only produce odd harmonics of the 800-nm driving field since this inversion symmetry between half-cycles of the 800-nm field is preserved.

In Fig. 2(a), we compare the harmonic yields of all single-color and two-color measurements. Furthermore, in Fig. 2(b) we compare the relative enhancement of HHG produced by the two-color and 266-nm driving fields with respect to the HHG yields produced by the 800-nm field. Note that for the two-color driving fields, we chose the phase between the two colors that optimizes the total yield for each individual harmonic.

First concentrating on the 800–400-nm two-color fields, the two intensity ratios we studied consisted of fields with 800- and 400-nm intensities of 1.3 and 2.0×10^{14} W/cm², or 1.3:2.0 respectively, as well as 3.5 and 1.0×10^{14} W/cm², or 3.5:1.0. Although we do not observe a two-order of magnitude enhancement as previously reported [31, 33], we do see a significant increase of photon flux compared to the single color 800-nm driving field. For photon energies less than approximately 35 eV, the two intensity ratios produce about the same photon flux, with an enhancement of 45 at 14.4 eV to 16 at 30 eV. A significant difference between the intensity ratios arises at photon energies larger than 35 eV, where the ratio of 3.5:1.0 dominates, maintaining about an order of magnitude enhancement over HHG driven by the 800-nm field. We believe that this is simply due to the increased intensity of the 800-nm field, leading to larger pondermotive energy and cutoff.

In Fig. 2(a), we also compare the total HHG yield driven by the two-color 800–400-nm fields to the single-color 400- and 266-nm fields. At similar photon energies below 25 eV, the single color 400-nm field produces approximately the same flux, within a factor of 2, as the two-color 800–400-nm driving fields. However, at similar energies larger than 25 eV, the two-color fields dominate. Again, we speculate that this is due to the enhancement of the cutoff photon energy in the two-color driving fields. On the other hand, the 266-nm driving field outperforms the two-color fields at 14.4 eV by about a factor of 50. However, due to the low cutoff of the 266-nm driving field, the 800–400-nm fields outperform the 266-nm field at 23.6 eV by about a factor of 10.

Now switching our focus to the 800–266-nm driving fields, we performed measurements using single-color intensity ratios of 1.3:1.0 and 3.0:0.4, where the intensities are in the 10^{14} W/cm² regime. Here, we observe that the 1.3:1.0 intensity ratio is generally equivalent to or outperforms the 3.0:0.4 intensity ratio, especially at lower photon energies. For example, at 14.4 eV, the 1.3:1.0 intensity ratio leads to approximately a factor of 40 larger harmonic yield than the 3.0:0.4 intensity ratio and 3800 times larger than the 800-nm field. For photon energies above 20 eV, both 800–266-nm intensity ratios perform approximately the same. Both intensity ratios also dominate at all photon energies compared to the single-color 800-nm driving field.

Comparing the 800–266-nm to the 800–400-nm driving fields, we find that for photon energies less than 20 eV, the 1.3:1.0 intensity ratio of the 800–266-nm driving field dominates. For photon energies larger than 20 eV, both two-color schemes are roughly equivalent, atleast within the

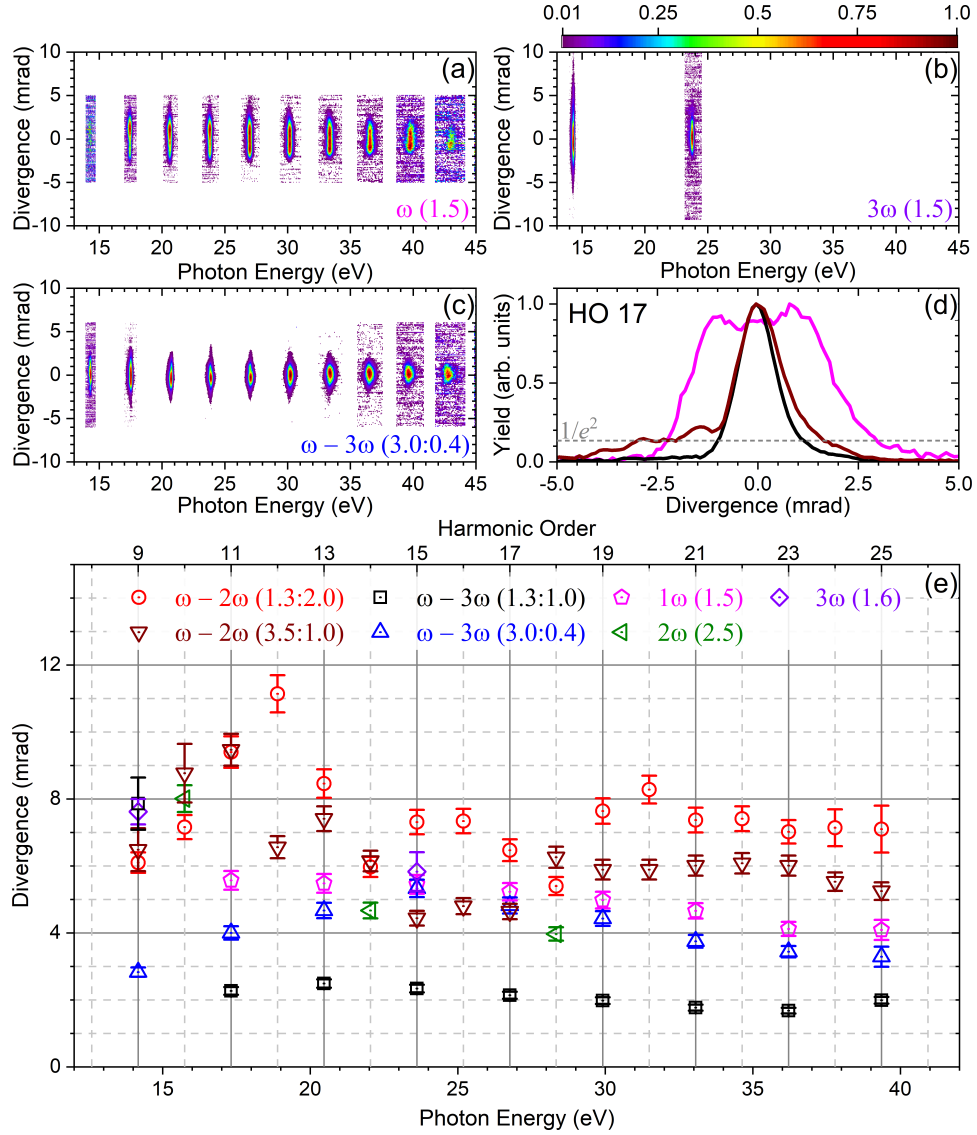


Fig. 3. The first three panels show the harmonic yield as a function of divergence angle and photon energy for the optimized (a) 800-nm (ω) field, (b) 266-nm (3ω) field, and the (c) 800-266-nm ($\omega - 3\omega$) field with intensity ratio of 3.0:0.4. Note, each individual harmonic is normalized such that the maximum pixel value is 1. (d) The projection of the harmonic 17 onto the divergence axis for the 800-nm, 800-400-nm field with intensity ratio of 3.5:1.0, and 800-266-nm field with intensity ratio of 1.3:1.0. The color coding of the plot follows the legend in panel (e) as well as the Fig. 2. Panel (e) shows the divergence for each harmonic for HHG driven by the single- and two-color driving fields. The divergence is defined as the $1/e^2$ full-width.

estimated errors of our measurements.

Performing a similar comparison between the 800-266-nm and 266-nm driving fields, we find that the two-color field with an intensity ratio of 1.3:1.0 is approximately the same as the single-color 266-nm field at 14.4 eV within our experimental error. On the other hand,

the single-color 266-nm driver produced about a factor of 25 more yield than the two-color 800–266-nm driving field with an intensity ratio of 3.0:0.4.

The photon yield is not the only characteristic that many experimentalists may consider when choosing an HHG scheme. In particular, the spatial quality and divergence of the resulting beams is also important. In Fig.3(a-c), we show the harmonic yields as a function of divergence angle and photon energies for the single-color 800-, 266-, and two-color 800–266-nm field with intensity ratio of 3.0:0.4 in units of 10^{14} W/cm². Furthermore, in Fig.3(e) we show the divergence of each harmonic generated by all single- and two-color driving schemes we discussed above. Note, we define the divergence as the $1/e^2$ full-width. We find that the 800–266-nm driving fields generally produces harmonics with smaller divergence angle than the optimized single-color and two-color 800–400-nm driving fields. For some harmonics, such as the 21st harmonic, the divergence for the 800–266-nm field with intensity ratio of 1.3:1.0 is more than two times smaller than the 800-nm field. For example, in Fig.3(d), we show the projections of the 17th harmonic for the 800-nm, 800–400-nm field with intensity ratio of 3.5:1.0, and 800–266-nm field with intensity ratio of 1.3:1.0. Note that to make this plot, we chose the intensity ratio that results in the narrowest distribution for each two-color combination. For the 17th harmonic, we find that the two-color fields produce a much narrower harmonic than the 800-nm driving field. Furthermore, we find that the 800–400-nm field contains some extra structure at larger divergence angles, effectively making the divergence larger than the 800–266-nm case. In certain applications, having a significantly narrower divergence angle will make the 800–266-nm driving fields preferable over their single- and two-color counterparts.

Our observation that $\omega - 3\omega$ fields have narrower divergence angles may suggest that we are selecting which electron trajectories are dominating the HHG. Recall, Jin *et al.* [40, 41] theoretically predicted that the $\omega - 3\omega$ laser fields produce a large enhancement because these two-color fields optimize the short over the long electron trajectories. Since the short electron trajectory harmonics usually dominate the total on-axis emitted power [53], our observation of significantly narrower divergence angles for the 800–266-nm fields may support their prediction.

5. Summary

In this paper, we compared the relative flux of HHG driven by the optimized single color 800-, 400-, and 266-nm driving fields to the two-color 800–400- and 800–266-nm driving fields. We found that, for photon energies below 20 eV, the 800–266-nm driving field with an intensity ratio of 1.3:1.0 significantly outperforms the other driving fields, with the exception of the 266-nm single-color field at 14.4 eV, where both fields produce approximately the same HHG yield. For common photon energies above 20 eV, all two-color driving fields produce approximately the same HHG yield. In addition, we discovered that the 800–266-nm driving field with an intensity ratio of 1.3:1.0 produces harmonics with significantly narrower divergence angle for photon energies above 15 eV compared to all other schemes.

The best generation scheme strongly depends on the application. For example, driving HHG with an 800–400-nm field may not be ideal when using a monochromator [50, 51] since the spacing between adjacent harmonics is smaller than the 800–266-nm case. When comparing the two-color driving fields to the single-color 400- and 266-nm fields, we find that these single-color fields are approximately equivalent in photon flux. Therefore, for applications where only these photon energies are needed, it is better to drive HHG with the single-color fields since they are easier to implement experimentally.

These results can help guide experimentalists identify which two-color or single-color harmonic generation scheme may better fit their experimental needs. It is worth noting that the HHG enhancement that we achieved may be improved upon by further optimizing the phase-matching conditions by, for example using gas cells or waveguides, fine tuning the intensity ratios, changing the generation medium, or improving the relative phase stability between the two-color fields.

We believe that HHG driven by two-color fields is a promising approach which deserves further investigation.

Funding

This work and T.S. were partially supported by the National Science Foundation under Award No. IIA-1430493. JRML personnel and operations were supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office for Science, U.S. Department of Energy under Award # DE-FG02-86ER13491. The HITS laser was mainly financed by NSF-MRI grant No: 1229672, with additional contributions from DOD-DURIP grant No. FA2386-12-1-3014 and DOE grant No. DE-FG02-86ER13491.

References

1. P. Salières, A. L'Huillier, P. Antoine, and M. Lewenstein, "Study of the spatial and temporal coherence of high-order harmonics," in *Advances In Atomic, Molecular, and Optical Physics*, (Elsevier, 1999), pp. 83–142.
2. M. Bellini, C. Lyngå, A. Tozzi, M. B. Gaarde, T. W. Hänsch, A. L'Huillier, and C.-G. Wahlström, "Temporal coherence of ultrashort high-order harmonic pulses," *Phys. Rev. Lett.* **81**, 297–300 (1998).
3. R. A. Bartels, A. Paul, H. Green, H. C. Kapteyn, M. M. Murnane, S. Backus, I. P. Christov, Y. Liu, D. Attwood, and C. Jacobsen, "Generation of spatially coherent light at extreme ultraviolet wavelengths," *Science* **297**, 376–378 (2002).
4. C. Benko, T. K. Allison, A. Cingöz, L. Hua, F. Labaye, D. C. Yost, and J. Ye, "Extreme ultraviolet radiation with coherence time greater than 1 s," *Nat. Photonics* **8**, 530–536 (2014).
5. J. Terschlüsen, M. Agåker, M. Svanqvist, S. Plogmaker, J. Nordgren, J.-E. Rubensson, H. Siegbahn, and J. Söderström, "Measuring the temporal coherence of a high harmonic generation setup employing a fourier transform spectrometer for the VUV/XUV," *Nucl. Instruments Methods Phys. Res. Sect. A: Accel. Spectrometers, Detect. Assoc. Equip.* **768**, 84–88 (2014).
6. S. Huang, Y. Ding, Y. Feng, E. Hemsing, Z. Huang, J. Krzywinski, A. Lutman, A. Marinelli, T. Maxwell, and D. Zhu, "Generating single-spike hard x-ray pulses with nonlinear bunch compression in free-electron lasers," *Phys. Rev. Lett.* **119** (2017).
7. R. N. Coffee, J. P. Cryan, J. Duris, W. Helml, S. Li, and A. Marinelli, "Development of ultrafast capabilities for x-ray free-electron lasers at the linac coherent light source," *Philos. Transactions Royal Soc. A: Math. Phys. Eng. Sci.* **377**, 20180386 (2019).
8. J. Duris, S. Li, T. Driver, E. G. Champenois, J. P. MacArthur, A. A. Lutman, Z. Zhang, P. Rosenberger, J. W. Aldrich, R. Coffee, G. Coslovich, F.-J. Decker, J. M. Glowina, G. Hartmann, W. Helml, A. Kamalov, J. Knurr, J. Krzywinski, M.-F. Lin, J. P. Marangos, M. Nantel, A. Natan, J. T. O'Neal, N. Shivaram, P. Walter, A. L. Wang, J. J. Welch, T. J. A. Wolf, J. Z. Xu, M. F. Kling, P. H. Bucksbaum, A. Zholents, Z. Huang, J. P. Cryan, and A. Marinelli, "Tunable isolated attosecond x-ray pulses with gigawatt peak power from a free-electron laser," *Nat. Photonics* (2019).
9. Z. Chang, *Fundamentals of Attosecond Optics* (CRC Press, 2011).
10. C. D. Lin, A.-T. Le, C. Jin, and H. Wei, *Attosecond and Strong-Field Physics* (Cambridge University Press, 2018).
11. E. Takahashi, Y. Nabekawa, and K. Midorikawa, "Generation of 10- μ j coherent extreme-ultraviolet light by use of high-order harmonics," *Opt. Lett.* **27**, 1920–1922 (2002).
12. S. Hädrich, J. Rothhardt, M. Krebs, S. Demmler, A. Klenke, A. Tünnermann, and J. Limpert, "Single-pass high harmonic generation at high repetition rate and photon flux," *J. Phys. B: At. Mol. Opt. Phys.* **49**, 172002 (2016).
13. C. M. Heyl, C. L. Arnold, A. Couairon, and A. L'Huillier, "Introduction to macroscopic power scaling principles for high-order harmonic generation," *J. Phys. B: At. Mol. Opt. Phys.* **50**, 013001 (2017).
14. I. Makos, I. Orfanos, A. Nayak, J. Peschel, B. Major, I. Lontos, E. Skantzakis, N. Papadakis, C. Kalpouzos, M. Dumergue, S. Kühn, K. Varju, P. Johnsson, A. L'Huillier, P. Tzallas, and D. Charalambidis, "A 10-gigawatt attosecond source for non-linear xuv optics and xuv-pump-xuv-probe studies," *Sci. Reports* **10**, 3759 (2020).
15. Y. Tamaki, J. Itatani, Y. Nagata, M. Obara, and K. Midorikawa, "Highly efficient, phase-matched high-harmonic generation by a self-guided laser beam," *Phys. Rev. Lett.* **82**, 1422–1425 (1999).
16. J. R. Sutherland, E. L. Christensen, N. D. Powers, S. E. Rhynard, J. C. Painter, and J. Peatross, "High harmonic generation in a semi-infinite gas cell," *Opt. Express* **12**, 4430 (2004).
17. P. Rudawski, C. M. Heyl, F. Brizuela, J. Schwenke, A. Persson, E. Mansten, R. Rakowski, L. Rading, F. Campi, B. Kim, P. Johnsson, and A. L'Huillier, "A high-flux high-order harmonic source," *Rev. Sci. Instruments* **84**, 073103 (2013).
18. H.-W. Sun, P.-C. Huang, Y.-H. Tzeng, J.-T. Huang, C. D. Lin, C. Jin, and M.-C. Chen, "Extended phase matching of high harmonic generation by plasma-induced defocusing," *Optica* **4**, 976 (2017).
19. A. Rundquist, C. G. Durfee, Z. Chang, C. Herne, S. Backus, M. M. Murnane, and H. C. Kapteyn, "Phase-matched generation of coherent soft x-rays," *Science* **280**, 1412–1415 (1998).
20. T. Pfeifer, R. Kemmer, R. Spitzenpfel, D. Walter, C. Winterfeldt, G. Gerber, and C. Spielmann, "Spatial control of high-harmonic generation in hollow fibers," *Opt. Lett.* **30**, 1497 (2005).

21. A. Paul, E. Gibson, X. Zhang, A. Lytle, T. Popmintchev, X. Zhou, M. Murnane, I. Christov, and H. Kapteyn, "Phase-matching techniques for coherent soft x-ray generation," *IEEE J. Quantum Electron.* **42**, 14–26 (2006).
22. T. Popmintchev, M.-C. Chen, A. Bahabad, M. Gerrity, P. Sidorenko, O. Cohen, I. P. Christov, M. M. Murnane, and H. C. Kapteyn, "Phase matching of high harmonic generation in the soft and hard x-ray regions of the spectrum," *Proc. Natl. Acad. Sci.* **106**, 10516–10521 (2009).
23. S. Adachi, T. Horio, and T. Suzuki, "Generation of intense single-order harmonic pulse in the vacuum ultraviolet region using a deep ultraviolet driving laser," *Opt. Lett.* **37**, 2118–2120 (2012).
24. D. Popmintchev, C. Hernández-García, F. Dollar, C. Mancuso, J. A. Pérez-Hernández, M.-C. Chen, A. Hankla, X. Gao, B. Shim, A. L. Gaeta, M. Tarazkar, D. A. Romanov, R. J. Levis, J. A. Gaffney, M. Foord, S. B. Libby, A. Jaron-Becker, A. Becker, L. Plaja, M. M. Murnane, H. C. Kapteyn, and T. Popmintchev, "Ultraviolet surprise: Efficient soft x-ray high-harmonic generation in multiply ionized plasmas," *Science* **350**, 1225–1231 (2015).
25. H. Wang, Y. Xu, S. Ulonska, J. S. Robinson, P. Ranitovic, and R. A. Kaindl, "Bright high-repetition-rate source of narrowband extreme-ultraviolet harmonics beyond 22 eV," *Nat. Commun.* **6** (2015).
26. C. Marceau, T. J. Hammond, A. Y. Naumov, P. B. Corkum, and D. M. Villeneuve, "Wavelength scaling of high harmonic generation for 267 nm, 400 nm and 800 nm driving laser pulses," *J. Phys. Commun.* **1**, 015009 (2017).
27. S. Adachi and T. Suzuki, "UV-driven harmonic generation for time-resolved photoelectron spectroscopy of polyatomic molecules," *Appl. Sci.* **8**, 1784 (2018).
28. S. Watanabe, K. Kondo, Y. Nabekawa, A. Sagisaka, and Y. Kobayashi, "Two-color phase control in tunneling ionization and harmonic generation by a strong laser field and its third harmonic," *Phys. Rev. Lett.* **73**, 2692–2695 (1994).
29. U. Andiel, G. D. Tsakiris, E. Cormier, and K. Witte, "High-order harmonic amplitude modulation in two-colour phase-controlled frequency mixing," *EPL (Europhysics Lett.)* **47**, 42 (1999).
30. E. Cormier and M. Lewenstein, "Optimizing the efficiency in high order harmonic generation optimization by two-color fields," *The Eur. Phys. J. D - At. Mol. Opt. Plasma Phys.* **12**, 227–233 (2000).
31. I. Kim, C. Kim, H. Kim, G. Lee, Y. Lee, J. Park, D. Cho, and C. Nam, "Highly efficient high-harmonic generation in an orthogonally polarized two-color laser field," *Phys. Rev. Lett.* **94**, 243901 (2005).
32. T. T. Liu, T. Kanai, T. Sekikawa, and S. Watanabe, "Significant enhancement of high-order harmonics below 10 nm in a two-color laser field," *Phys. Rev. A* **73**, 063823 (2006).
33. I. J. Kim, G. H. Lee, S. B. Park, Y. S. Lee, T. K. Kim, C. H. Nam, T. Mocek, and K. Jakubczak, "Generation of submicrojoule high harmonics using a long gas jet in a two-color laser field," *Appl. Phys. Lett.* **92**, 021125 (2008).
34. G. Lambert, J. Gautier, C. P. Hauri, P. Zeitoun, C. Valentin, T. Marchenko, F. Tissandier, J. P. Goddet, M. Ribiere, G. Rey, M. Fajardo, and S. Sebban, "An optimized kHz two-colour high harmonic source for seeding free-electron lasers and plasma-based soft x-ray lasers," *New J. Phys.* **11**, 083033 (2009).
35. L. Brugnera, F. Frank, D. J. Hoffmann, R. Torres, T. Siegel, J. G. Underwood, E. Springate, C. Froud, E. I. C. Turcu, J. W. G. Tisch, and J. P. Marangos, "Enhancement of high harmonics generated by field steering of electrons in a two-color orthogonally polarized laser field," *Opt. Lett.* **35**, 3994–3996 (2010).
36. T. Siegel, R. Torres, D. J. Hoffmann, L. Brugnera, I. Procino, A. Zaïr, J. G. Underwood, E. Springate, I. C. E. Turcu, L. E. Chipperfield, and J. P. Marangos, "High harmonic emission from a superposition of multiple unrelated frequency fields," *Opt. Express* **18**, 6853–6862 (2010).
37. P. Wei, J. Miao, Z. Zeng, C. Li, X. Ge, R. Li, and Z. Xu, "Selective enhancement of a single harmonic emission in a driving laser field with subcycle waveform control," *Phys. Rev. Lett.* **110**, 233903 (2013).
38. F. Brizuela, C. M. Heyl, P. Rudawski, D. Kroon, L. Rading, J. M. Dahlström, J. Mauritsson, P. Johnsson, C. L. Arnold, and A. L'Huillier, "Efficient high-order harmonic generation boosted by below-threshold harmonics," *Sci. Rep.* **3**, 1410 (2013).
39. P. Wei, Z. Zeng, J. Jiang, J. Miao, Y. Zheng, X. Ge, C. Li, and R. Li, "Selective generation of an intense single harmonic from a long gas cell with loosely focusing optics based on a three-color laser field," *Appl. Phys. Lett.* **104**, 151101 (2014).
40. C. Jin, G. Wang, H. Wei, A.-T. Le, and C. D. Lin, "Waveforms for optimal sub-keV high-order harmonics with synthesized two- or three-colour laser fields," *Nat Commun* **5**, – (2014).
41. C. Jin, G. Wang, A.-T. Le, and C. D. Lin, "Route to optimal generation of soft x-ray high harmonics with synthesized two-color laser pulses," *Sci. Reports* **4**, 7067– (2014).
42. S. Haessler, T. Balčiūnas, G. Fan, G. Andriukaitis, A. Pugžlys, A. Baltuška, T. Witting, R. Squibb, A. Zaïr, J. W. G. Tisch, J. P. Marangos, and L. E. Chipperfield, "Optimization of quantum trajectories driven by strong-field waveforms," *Phys. Rev. X* **4**, 021028 (2014).
43. C. Jin, K.-H. Hong, and C. D. Lin, "Optimal generation of high harmonics in the water-window region by synthesizing 800-nm and mid-infrared laser pulses," *Opt. Lett.* **40**, 3754–3757 (2015).
44. T. Kroh, C. Jin, P. Krogen, P. D. Keathley, A.-L. Calendron, J. P. Siqueira, H. Liang, E. L. Falcão-Filho, C. D. Lin, F. X. Kärtner, and K.-H. Hong, "Enhanced high-harmonic generation up to the soft x-ray region driven by mid-infrared pulses mixed with their third harmonic," *Opt. Express* **26**, 16955 (2018).
45. M. Sayrac, A. A. Kolomenskii, J. Dong, and H. A. Schuessler, "Generation of enhanced even harmonics of fundamental radiation in temporally separated two-color laser fields," *J. Electron Spectrosc. Relat. Phenom.* **233**, 22–27 (2019).
46. A. Comby, D. Descamps, S. Beauvarlet, A. Gonzalez, F. Guichard, S. Petit, Y. Zaouter, and Y. Mairesse, "Cascaded

- harmonic generation from a fiber laser: a milliwatt XUV source,” *Opt. Express* **27**, 20383 (2019).
47. B. Langdon, J. Garlick, X. Ren, D. J. Wilson, A. M. Summers, S. Zigo, M. F. Kling, S. Lei, C. G. Elles, E. Wells, E. D. Poliakoff, K. D. Carnes, V. Kumarappan, I. Ben-Itzhak, and C. A. Trallero-Herrero, “Carrier-envelope-phase stabilized terawatt class laser at 1 khz with a wavelength tunable option,” *Opt. Express* **23**, 4563–4572 (2015).
 48. C. Martin and S. Bowyer, “Quantum efficiency of opaque CsI photocathodes with channel electron multiplier arrays in the extreme and far ultraviolet,” *Appl. Opt.* **21**, 4206 (1982).
 49. R. Trebino, K. W. DeLong, D. N. Fittinghoff, J. N. Sweetser, M. A. Krumbügel, B. A. Richman, and D. J. Kane, “Measuring ultrashort laser pulses in the time-frequency domain using frequency-resolved optical gating,” *Rev. Sci. Instruments* **68**, 3277–3295 (1997).
 50. L. Nugent-Glandorf, M. Scheer, M. Krishnamurthy, J. W. Odom, and S. R. Leone, “Photoelectron spectroscopic determination of the energy bandwidths of high-order harmonics (7th–55th) produced by an ultrafast laser in neon,” *Phys. Rev. A* **62** (2000).
 51. F. Frassetto, C. Cacho, C. A. Froud, I. E. Turcu, P. Villoresi, W. A. Bryan, E. Springate, and L. Poletto, “Single-grating monochromator for extreme-ultraviolet ultrashort pulses,” *Opt. Express* **19**, 19169 (2011).
 52. N. Dudovich, O. Smirnova, J. Levesque, Y. Mairesse, M. Y. Ivanov, D. M. Villeneuve, and P. B. Corkum, “Measuring and controlling the birth of attosecond xuv pulses,” *Nat Phys* **2**, 781–786 (2006).
 53. L. Brugnera, D. J. Hoffmann, T. Siegel, F. Frank, A. Zair, J. W. G. Tisch, and J. P. Marangos, “Trajectory selection in high harmonic generation by controlling the phase between orthogonal two-color fields,” *Phys. Rev. Lett.* **107**, 153902 (2011).

6.5 Summary and outlook

In this Chapter, we explored the enhancement of HHG using two-color driving-fields as compared to their single-color counterparts. We determined that harmonics produced by the two-color driving fields generally outperform the single-color 800-nm driving field by one to three orders of magnitude. Furthermore, in the $\omega - 3\omega$ case, we showed that we can control, by changing intensity ratios, whether the ionization rate or the diffusion of electron wavepacket plays a larger role in enhancing HHG. Furthermore, we showed that the 800–266-nm driving fields tend to produce harmonics with much smaller divergence angles, suggesting they significantly enhance the contributions of the short trajectories compared to the other generation methods. By minimizing the long trajectories’ contributions, we improve the wavefront and coherence of the resulting photon beam [253], providing experimentalists a better photon source.

Hopefully, our results will help experimentalists choose the generation schemes that are right for their specific applications. Furthermore, we think our results may be improved upon to reach the enhancements theoretically predicted by Jin *et al.*[247]. One method is to explore different generation media, such as gas cells [240–243] or waveguides [232, 244], which may boost the macroscopic conversion efficiency and further enhance the harmonics. Alternatively, our results can be further improved by finding an intensity ratio between the $\omega - 3\omega$ fields which simultaneously minimizes the electron’s excursion time while maximizing the ionization rate for the short trajectories. Finally, our results demonstrating that the $\omega - 3\omega$ fields can control the excursion times of electron trajectories by a factor of 2 are useful for methods which use the returning electron wavepacket as a probe, such as high-harmonic spectroscopy [213, 254–259] and laser-induced electron diffraction [2, 223–225]. In the future, we hope to use this improved light source as a probe for studying molecular fragmentation dynamics.

Chapter 7

Summary and Outlook

Throughout this dissertation, we aimed to improve our understanding of molecular fragmentation dynamics. We approached this problem from several fronts, mainly by using coincidence three-dimensional momentum imaging techniques to study the physical processes of molecular fragmentation and by improving our experimental capabilities to enable the exploration of new questions. Our main findings and their contributions to the broad research community are summarized below.

My works' main contribution to the broad research community was the development of the native frames method for analyzing multi-body fragmentation. Specifically, we used the conjugate momenta of Jacobi coordinates to reduce the dimensionality of the measured momentum distribution, providing us with a general method to analyze multi-body fragmentation. Furthermore, we applied the method to identify sequential fragmentation by using the rotation of the intermediate product in the fragmentation plane as a signature¹. We then extend the method to separate sequential from concerted breakup in any plot created from the measured momenta. In addition, we identified the states involved in each fragmentation step, at least in certain circumstances. Finally, we explored the limitation of our analysis and extended it to four-body breakup.

The broader implication of our native-frames work is that we can remove contributions

¹The additional criteria is that populated state's lifetime is much longer than its rotational period. Also, in some cases, other signatures can be used instead.

of sequential fragmentation from the data, at least under certain conditions. This accomplishment is important because researchers commonly invoke the axial-recoil approximation to interpret the concerted fragmentation dynamics. By eliminating sequential fragmentation, we remove the most egregious violation of this approximation. In addition, the native frames analysis approach provides researchers with a general framework for analyzing multi-body fragmentation. Finally, as higher efficiency detectors and higher repetition rate photon sources become widely available, researchers move toward studying four or more body fragmentation. Therefore, it is important to develop analysis methods that can identify and potentially separate competing multi-body fragmentation processes. In the future, we hope to realize these benefits and explore some of the more exotic sequential fragmentation pathways that may occur in four or more body breakup.

We also presented our studies on isomerization and hydrogen roaming in this thesis. We demonstrated that isomerization can occur following the double ionization of several tri-atomic molecules, leading to fragmentation channels where the two “edge” atoms form a new molecule. Specifically, we showed that the branching ratio of these bond-rearrangement channels tend to be approximately 0.1% of all possible one-, two-, and three-body channels resulting from double ionization. This result demonstrated that such channels need to be generally considered, for example, as potential candidates leading to sequential fragmentation, even though they typically have a low formation probability. We also explored how molecular hydrogen roaming contributes to the formation of H_3^+ ions from various alcohol molecules. This result shows that roaming, which is generally studied as occurring in neutral molecules, may also occur in higher charge states. In the future, we hope to expand our studies in ethanol, specifically trying to determine the influences of the different hydrogen sites on the total H_3^+ formation probability.

The final set of “molecular dynamics” experiments focused on the coherent control of molecular ions. In particular, we demonstrated that a pump-dump-like transition can occur in the CS^{2+} molecules, where the molecules may fragment without gaining significant energy from the laser field. Since many dicationic potential energy surfaces share similar characteristics to CS^{2+} , namely a large potential barrier allowing the molecule to stay “bound”

followed by a Coulomb repulsion tail, such pump-dump-like transitions can generally occur. Furthermore, we observed attosecond time-delays between different initial vibrational levels in the two-color driven dissociation of D_2^+ molecular ions. This result demonstrates that such time-delays (phase shifts) can be measured, enabling possible extensions to other systems where we can study attosecond time-delays in the nuclear motion within the molecule, i.e. independent of electron dynamics.

Finally, we made several technical improvements to enable future experiments studying molecular dynamics. First, we upgraded our molecular-ion beam momentum imaging setup to enable measurements of breakup channels where the fragments have large differences in their mass-to-charge ratios. Specifically, we added a second movable detector to measure the light ionic fragments, such as H^+ and D^+ , and presented preliminary data focused on the fragmentation of CD_2^+ . This setup enables, for example, the study of hydrogen versus proton elimination from hydrocarbons, the ejection of neutral H_2 from alcohol molecules which is a necessary precursor to H_3^+ formation due to its roaming, and even four or more body sequential fragmentation dynamics.

Our second technical improvement was enhancing photon flux from high-order harmonic generation driven by two-color laser fields. In particular, we showed that two-color 800–400-nm and 800–266-nm driving fields can enhance the harmonic photon flux by more than one order of magnitude compared to the single-color 800-nm driving field. Furthermore, we showed that the 800–266-nm driving fields produce harmonics with narrower divergence angles, suggesting that we enhanced the contribution of the so-called “short” compared to the “long” electron trajectories, improving the quality of the photon source that we hope to use for probing molecular dynamics. Finally, we also demonstrated that we can control the excursion times of the “short” electron trajectories by as much as a factor of two using the 800–266-nm driving fields. This result is important for methods using the rescattering electron wavepacket as a probe of molecular dynamics, such as in high harmonic spectroscopy and laser induced electron diffraction (LIED).

Collectively, this thesis has explored and made progress in addressing many questions related to molecular fragmentation dynamics. Many of the developments and contributions

presented throughout the thesis open new doors and introduce further questions to be explored in the future.

Bibliography

- [1] Z. Chang, *Fundamentals of Attosecond Optics* (CRC Press, 2011).
- [2] C. D. Lin, A.-T. Le, C. Jin, and H. Wei, *Attosecond and Strong-Field Physics* (Cambridge University Press, 2018).
- [3] G. Steinmeyer, *Journal of Optics A: Pure and Applied Optics* **5**, R1 (2002).
- [4] K. Codling and L. J. Frasinski, *Journal of Physics B: Atomic, Molecular and Optical Physics* **26**, 783 (1993).
- [5] A. Giusti-Suzor, F. H. Mies, L. F. DiMauro, E. Charron, and B. Yang, *Journal of Physics B: Atomic, Molecular and Optical Physics* **28**, 309 (1995).
- [6] J. H. Posthumus, *Reports on Progress in Physics* **67**, 623 (2004).
- [7] J. Ullrich, R. Moshhammer, R. Dörner, O. Jagutzki, V. Mergel, H. Schmidt-Böcking, and L. Spielberger, *Journal of Physics B: Atomic, Molecular and Optical Physics* **30**, 2917 (1997).
- [8] R. Dörner, V. Mergel, O. Jagutzki, L. Spielberger, J. Ullrich, R. Moshhammer, and H. Schmidt-Böcking, *Physics Reports* **330**, 95 (2000).
- [9] J. Ullrich, R. Moshhammer, A. Dorn, R. D orner, L. P. H. Schmidt, and H. Schmidt-Böcking, *Reports on Progress in Physics* **66**, 1463 (2003).
- [10] T. Jahnke, T. Weber, T. Osipov, A. Landers, O. Jagutzki, L. Schmidt, C. Cocke, M. Prior, H. Schmidt-Böcking, and R. D orner, *Journal of Electron Spectroscopy and Related Phenomena* **141**, 229 (2004).

- [11] I. Ben-Itzhak, P. Q. Wang, J. F. Xia, A. M. Sayler, M. A. Smith, K. D. Carnes, and B. D. Esry, *Phys. Rev. Lett.* **95**, 073002 (2005).
- [12] D. Reedy, J. B. Williams, B. Gaire, A. Gatton, M. Weller, A. Menssen, T. Bauer, K. Henrichs, P. Burzynski, B. Berry, et al., *Physical Review A* **98**, 053430 (2018).
- [13] Z. L. Streeter, F. L. Yip, R. R. Lucchese, B. Gervais, T. N. Rescigno, and C. W. McCurdy, *Physical Review A* **98**, 053429 (2018).
- [14] C. J. Joachain, N. J. Kylstra, and R. M. Potvliege, *Atoms in Intense Laser Fields* (Cambridge University Press, 2009).
- [15] S. Stenholm, *Contemporary Physics* **20**, 37 (1979).
- [16] A. J. Bain, in *Photonics* (John Wiley & Sons, Inc., 2015), p. 279.
- [17] P. Agostini, F. Fabre, G. Mainfray, G. Petite, and N. K. Rahman, *Physical Review Letters* **42**, 1127 (1979).
- [18] K. Bergmann, N. V. Vitanov, and B. W. Shore, *The Journal of Chemical Physics* **142**, 170901 (2015).
- [19] N. V. Vitanov, A. A. Rangelov, B. W. Shore, and K. Bergmann, *Reviews of Modern Physics* **89**, 015006 (2017).
- [20] R. R. Freeman, P. H. Bucksbaum, H. Milchberg, S. Darack, D. Schumacher, and M. E. Geusic, *Physical Review Letters* **59**, 1092 (1987).
- [21] B. Walker, B. Sheehy, L. F. DiMauro, P. Agostini, K. J. Schafer, and K. C. Kulander, *Physical Review Letters* **73**, 1227 (1994).
- [22] P. H. Bucksbaum, A. Zavriyev, H. G. Muller, and D. W. Schumacher, *Physical Review Letters* **64**, 1883 (1990).
- [23] A. M. Weiner, *Ultrafast Optics* (Wiley, 2009).

- [24] A. H. Zewail, *Science* **242**, 1645 (1988).
- [25] A. Mokhtari, P. Cong, J. L. Herek, and A. H. Zewail, *Nature* **348**, 225 (1990).
- [26] N. E. Henriksen and V. Engel, *International Reviews in Physical Chemistry* **20**, 93 (2001).
- [27] M. Fushitani, *Annual Reports Section C: (Physical Chemistry)* **104**, 272 (2008).
- [28] A. H. Zewail, *Angewandte Chemie International Edition* **39**, 2586 (2000).
- [29] P. B. Corkum and F. Krausz, *Nature Physics* **3**, 381 (2007).
- [30] F. Lepine, M. Y. Ivanov, and M. J. J. Vrakking, *Nat Photon* **8**, 195 (2014).
- [31] M. Nisoli, P. Decleva, F. Calegari, A. Palacios, and F. Martín, *Chemical Reviews* **117**, 10760 (2017).
- [32] R. J. Gordon, L. Zhu, and T. Seideman, *Accounts of Chemical Research* **32**, 1007 (1999).
- [33] C. Brif, R. Chakrabarti, and H. Rabitz, *New Journal of Physics* **12**, 075008 (2010).
- [34] M. Shapiro and P. Brumer, *Quantum Control of Molecular Processes* (Wiley, 2012).
- [35] G. E. Hall and P. L. Houston, *Annual Review of Physical Chemistry* **40**, 375 (1989).
- [36] A. J. R. Heck and D. W. Chandler, *Annual Review of Physical Chemistry* **46**, 335 (1995).
- [37] R. E. Continetti, *Annual Review of Physical Chemistry* **52**, 165 (2001).
- [38] B. Whitaker, ed., *Imaging in Molecular Dynamics - Technology and Applications* (Cambridge University Press, New York, NY, 2003).
- [39] A. M. Sayler, Ph.D. thesis, Kansas State University (2008).
- [40] B. Gaire, Ph.D. thesis, Kansas State University (2011).

- [41] P. Q. Wang, A. M. Sayler, K. D. Carnes, J. F. Xia, M. A. Smith, B. D. Esry, and I. Ben-Itzhak, *Physical Review A* **74**, 043411 (2006).
- [42] J. McKenna, A. M. Sayler, F. Anis, B. Gaire, N. G. Johnson, E. Parke, J. J. Hua, H. Mashiko, C. M. Nakamura, E. Moon, et al., *Physical Review Letters* **100**, 133001 (2008).
- [43] J. McKenna, F. Anis, B. Gaire, N. G. Johnson, M. Zohrabi, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Physical Review Letters* **103**, 103006 (2009).
- [44] J. McKenna, A. M. Sayler, B. Gaire, N. G. Johnson, M. Zohrabi, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Journal of Physics B: Atomic, Molecular and Optical Physics* **42**, 121003 (2009).
- [45] N. G. Kling, K. J. Betsch, M. Zohrabi, S. Zeng, F. Anis, U. Ablikim, B. Jochim, Z. Wang, M. Kübel, M. F. Kling, et al., *Physical Review Letters* **111**, 163004 (2013).
- [46] J. McKenna, A. M. Sayler, B. Gaire, N. G. Johnson, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Physical Review Letters* **103**, 103004 (2009).
- [47] A. M. Sayler, J. McKenna, B. Gaire, N. G. Kling, K. D. Carnes, and I. Ben-Itzhak, *Physical Review A* **86**, 033425 (2012).
- [48] B. Gaire, J. McKenna, M. Zohrabi, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Physical Review A* **85**, 023419 (2012).
- [49] A. M. Sayler, J. McKenna, B. Gaire, N. G. Kling, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Journal of Physics B: Atomic, Molecular and Optical Physics* **47**, 031001 (2014).
- [50] B. Gaire, J. McKenna, A. M. Sayler, N. G. Johnson, E. Parke, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Physical Review A* **78**, 033430 (2008).
- [51] J. McKenna, A. M. Sayler, B. Gaire, N. G. Johnson, E. Parke, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Physical Review A* **77**, 063422 (2008).

- [52] J. McKenna, A. M. Sayler, F. Anis, N. G. Johnson, B. Gaire, U. Lev, M. A. Zohrabi, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, *Physical Review A* **81**, 061401(R) (2010).
- [53] M. Zohrabi, J. McKenna, B. Gaire, N. G. Johnson, K. D. Carnes, S. De, I. A. Bocharova, M. Magrakvelidze, D. Ray, I. V. Litvinyuk, et al., *Physical Review A* **83**, 053405 (2011).
- [54] L. Graham, M. Zohrabi, B. Gaire, U. Ablikim, B. Jochim, B. Berry, T. Severt, K. J. Betsch, A. M. Summers, U. Lev, et al., *Physical Review A* **91**, 023414 (2015).
- [55] B. Jochim, B. Berry, T. Severt, P. Feizollah, M. Zohrabi, Kanaka Raju P., E. Wells, K. D. Carnes, and I. Ben-Itzhak, *The Journal of Physical Chemistry Letters* **10**, 2320 (2019).
- [56] B. Jochim, M. Zohrabi, T. Severt, B. Berry, K. J. Betsch, P. Feizollah, J. Rajput, E. Wells, K. D. Carnes, and I. Ben-Itzhak, *Physical Review A* **101**, 013406 (2020).
- [57] C. E. M. Strauss and P. L. Houston, *The Journal of Physical Chemistry* **94**, 8751 (1990).
- [58] C. Maul and K.-H. Gericke, *International Reviews in Physical Chemistry* **16**, 1 (1997).
- [59] N. Neumann, D. Hant, L. P. H. Schmidt, J. Titze, T. Jahnke, A. Czasch, M. S. Schöffler, K. Kreidi, O. Jagutzki, H. Schmidt-Böcking, et al., *Phys. Rev. Lett.* **104**, 103201 (2010).
- [60] J. Rajput, T. Severt, B. Berry, B. Jochim, P. Feizollah, B. Kaderiya, M. Zohrabi, U. Ablikim, F. Ziaee, K. Raju P., et al., *Phys. Rev. Lett.* **120**, 103001 (2018).
- [61] S. Zhao, B. Jochim, P. Feizollah, J. Rajput, F. Ziaee, Kanaka Raju P., B. Kaderiya, K. Borne, Y. Malakar, B. Berry, et al., *Physical Review A* (2019).
- [62] G. L. Glish and R. W. Vachet, *Nature Reviews Drug Discovery* **2**, 140 (2003).

- [63] H. Awad, M. M. Khamis, and A. El-Aneed, *Applied Spectroscopy Reviews* **50**, 158 (2014).
- [64] R. G. Cooks and X. Yan, *Annual Review of Analytical Chemistry* **11**, 1 (2018).
- [65] P. L. Urban, Y.-C. Chen, and Y.-S. Wang, *Time-Resolved Mass Spectrometry: From Concept to Applications* (Wiley, 2016).
- [66] T. A. Carlson, *Annual Review of Physical Chemistry* **26**, 211 (1975).
- [67] F. Reinert and S. Hübner, *New Journal of Physics* **7**, 97 (2005).
- [68] B. Lv, T. Qian, and H. Ding, *Nature Reviews Physics* **1**, 609 (2019).
- [69] G. Greczynski and L. Hultman, *Progress in Materials Science* **107**, 100591 (2020).
- [70] D. M. Neumark, *Annual Review of Physical Chemistry* **52**, 255 (2001).
- [71] A. Stolow, A. E. Bragg, and D. M. Neumark, *Chemical Reviews* **104**, 1719 (2004).
- [72] D. W. Chandler and P. L. Houston, *The Journal of Chemical Physics* **87**, 1445 (1987).
- [73] A. T. J. B. Eppink and D. H. Parker, *Review of Scientific Instruments* **68**, 3477 (1997).
- [74] D. H. Parker and A. T. J. B. Eppink, in *Imaging in Molecular Dynamics* (Cambridge University Press, 2003), p. 20.
- [75] D. M. Neumark, *The Journal of Physical Chemistry A* **112**, 13287 (2008).
- [76] L. J. Frasinsik, K. Codling, and P. A. Hatherly, *Science* **246**, 1029 (1989).
- [77] L. J. Frasinski, *Journal of Physics B: Atomic, Molecular and Optical Physics* **49**, 152004 (2016).
- [78] C. Vallance, D. Heathcote, and J. W. L. Lee, *The Journal of Physical Chemistry A* **125**, 1117 (2021).
- [79] R. D. Hudson, *Reviews of Geophysics* **9**, 305 (1971).

- [80] W. Demtröder, *Laser Spectroscopy* (Springer-Verlag GmbH, 2008).
- [81] R. Geneaux, H. J. B. Marroux, A. Guggenmos, D. M. Neumark, and S. R. Leone, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences **377**, 20170463 (2019).
- [82] J. D. Roberts, Journal of Chemical Education **38**, 581 (1961).
- [83] H. Gunther, *NMR Spectroscopy: Basic principles, concepts, and applications in chemistry* (Wiley, 2013).
- [84] R. L. Hilderbrandt and R. A. Bonham, Annual Review of Physical Chemistry **22**, 279 (1971).
- [85] A. H. Zewail, Annual Review of Physical Chemistry **5**, 65 (2006).
- [86] A. A. Ishchenko, S. A. Aseyev, V. N. Bagratashvili, V. Y. Panchenko, and E. A. Ryabov, Physics-Uspekhi **57**, 633 (2014).
- [87] J. Yang and M. Centurion, Structural Chemistry **26**, 1513 (2015).
- [88] M. Gemmi, E. Mugnaioli, T. E. Gorelik, U. Kolb, L. Palatinus, P. Boullay, S. Hovmöller, and J. P. Abrahams, ACS Central Science **5**, 1315 (2019).
- [89] A. Ponce, J. A. Aguilar, J. Tate, and M. J. Yacamán, Nanoscale Advances **3**, 311 (2021).
- [90] P. Thibault and V. Elser, Annual Review of Condensed Matter Physics **1**, 237 (2010).
- [91] E. S. Ameh, The International Journal of Advanced Manufacturing Technology **105**, 3289 (2019).
- [92] K. Bennett, M. Kowalewski, J. R. Rouxel, and S. Mukamel, Proceedings of the National Academy of Sciences **115**, 6538 (2018).
- [93] T. Kierspel, A. Morgan, J. Wiese, T. Mullins, A. Aquila, A. Barty, R. Bean, R. Boll, S. Boutet, P. Bucksbaum, et al., The Journal of Chemical Physics **152**, 084307 (2020).

- [94] C. Pellegrini, *Physica Scripta* **T169**, 014004 (2016).
- [95] E. A. Seddon, J. A. Clarke, D. J. Dunning, C. Masciovecchio, C. J. Milne, F. Parmigiani, D. Rugg, J. C. H. Spence, N. R. Thompson, K. Ueda, et al., *Reports on Progress in Physics* **80**, 115901 (2017).
- [96] T. Tanaka, *Journal of Optics* **19**, 093001 (2017).
- [97] S. Pathak, L. M. Ibele, R. Boll, C. Callegari, A. Demidovich, B. Erk, R. Feifel, R. Forbes, M. D. Fraia, L. Giannessi, et al., *Nature Chemistry* **12**, 795 (2020).
- [98] S. Backus, C. G. Durfee, M. M. Murnane, and H. C. Kapteyn, *Review of Scientific Instruments* **69**, 1207 (1998).
- [99] K. Wille, *Reports on Progress in Physics* **54**, 1005 (1991).
- [100] D. H. Bilderback, P. Elleaume, and E. Weckert, *Journal of Physics B: Atomic, Molecular and Optical Physics* **38**, S773 (2005).
- [101] R. Trebino, K. W. DeLong, D. N. Fittinghoff, J. N. Sweetser, M. A. Krumbügel, B. A. Richman, and D. J. Kane, *Review of Scientific Instruments* **68**, 3277 (1997).
- [102] D. R. Miller, *Atomic and Molecular Beam Methods*, vol. 1 (Oxford University Press, 1988).
- [103] H. Pauly, *Atom, Molecule, and Cluster Beams I* (Springer, 2000).
- [104] N. G. Kling, Ph.D. thesis, Kansas State University (2013).
- [105] M. Zohrabi, Ph.D. thesis, Kansas State University (2014).
- [106] B. Berry, Ph.D. thesis, Kansas State University (2018).
- [107] B. Jochim, Ph.D. thesis, Kansas State University (2019).
- [108] S. F. Perry, *Industrial & Engineering Chemistry* **44**, 2037 (1952).

- [109] H. F. Schaefer, *Accounts of Chemical Research* **12**, 288 (1979).
- [110] R. P. Duran, V. T. Amorebieta, and A. J. Colussi, *Journal of the American Chemical Society* **109**, 3154 (1987).
- [111] F. Gai, *Science* **279**, 1886 (1998).
- [112] S. Allmann and I. T. Baldwin, *Science* **329**, 1075 (2010).
- [113] J. A. DeVine, M. L. Weichman, B. Laws, J. Chang, M. C. Babin, G. Balerdi, C. Xie, C. L. Malbon, W. C. Lineberger, D. R. Yarkony, et al., *Science* **358**, 336 (2017).
- [114] W. Domcke, D. R. Yarkony, and H. Köppel, *Conical Intersections* (WORLD SCIENTIFIC, 2004).
- [115] S. Matsika and P. Krause, *Annual Review of Physical Chemistry* **62**, 621 (2011).
- [116] W. Domcke and D. R. Yarkony, *Annual Review of Physical Chemistry* **63**, 325 (2012).
- [117] L. Shen, B. Xie, Z. Li, L. Liu, G. Cui, and W.-H. Fang, *The Journal of Physical Chemistry Letters* **11**, 8490 (2020).
- [118] P. M. Kroger and S. J. Riley, *The Journal of Chemical Physics* **67**, 4483 (1977).
- [119] B. K. Venkataraman, G. Bandukwalla, Z. Zhang, and M. Vernon, *The Journal of Chemical Physics* **90**, 5510 (1989).
- [120] S. Hsieh and J. H. D. Eland, *Journal of Physics B: Atomic, Molecular and Optical Physics* **30**, 4515 (1997).
- [121] A. Hishikawa, H. Hasegawa, and K. Yamanouchi, *Chemical Physics Letters* **361**, 245 (2002).
- [122] J. D. Savee, V. A. Mozhayskiy, J. E. Mann, A. I. Krylov, and R. E. Continetti, *Science* **321**, 826 (2008).

- [123] R. Dalitz, The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science **44**, 1068 (1953).
- [124] R. N. Zare, The Journal of Chemical Physics **47**, 204 (1967).
- [125] R. R. Lucchese, A. Lafosse, J. C. Brenot, P. M. Guyon, J. C. Houver, M. Lebech, G. Raseev, and D. Dowek, Physical Review A **65**, 020702(R) (2002).
- [126] D. Dowek, M. Lebech, J. Houver, and R. Lucchese, Journal of Electron Spectroscopy and Related Phenomena **141**, 211 (2004).
- [127] D. Toffoli, R. R. Lucchese, M. Lebech, J. C. Houver, and D. Dowek, The Journal of Chemical Physics **126**, 054307 (2007).
- [128] R. Guillemin, P. Decleva, M. Stener, C. Bomme, T. Marin, L. Journal, T. Marchenko, R. K. Kushawaha, K. Jänkälä, N. Trcera, et al., Nature Communications **6**, 6166 (2015).
- [129] G. Turri, P. Bolognesi, H. Sugimoto, J. Mathis, and L. Avaldi, Journal of Physics B: Atomic, Molecular and Optical Physics **52**, 07LT01 (2019).
- [130] J. M. Randazzo, G. Turri, P. Bolognesi, J. Mathis, L. U. Ancarani, and L. Avaldi, Physical Review A **101**, 033407 (2020).
- [131] R. N. Zare, Molecular Photochemistry **4**, 1 (1972).
- [132] T. P. Rakitzis and R. N. Zare, The Journal of Chemical Physics **110**, 3341 (1999).
- [133] S. Pathak, R. Obaid, S. Bhattacharyya, J. Bürger, X. Li, J. Tross, T. Severt, B. Davis, R. C. Bilodeau, C. A. Trallero-Herrero, et al., The Journal of Physical Chemistry Letters **11**, 10205 (2020).
- [134] S. T. Rittenhouse, J. von Stecher, J. P. D’Incao, N. P. Mehta, and C. H. Greene, Journal of Physics B: Atomic, Molecular and Optical Physics **44**, 172001 (2011).
- [135] T. A. Field and J. H. Eland, Chemical Physics Letters **211**, 4362 (1993).

- [136] M. Hochlaf, F. R. Bennett, G. Chambaud, and P. Rosmus, *Journal of Physics B: Atomic, Molecular and Optical Physics* **31**, 2163 (1998).
- [137] A. E. Slattery, T. A. Field, M. Ahmad, R. I. Hall, J. Lambourne, F. Penent, P. Lablanquie, and J. H. D. Eland, *The Journal of Chemical Physics* **122**, 084317 (2005).
- [138] V. Sharma, B. Bapat, J. Mondal, M. Hochlaf, K. Giri, and N. Sathyamurthy, *The Journal of Physical Chemistry A* **111**, 10205 (2007).
- [139] D. Zhang, B.-Z. Chen, M.-B. Huang, Q. Meng, and Z. Tian, *The Journal of Chemical Physics* **139**, 174305 (2013).
- [140] T. Ng and S. Bell, *Journal of Molecular Spectroscopy* **50**, 166 (1974).
- [141] C. Fridh, *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics* **74**, 190 (1978).
- [142] L. M. Beaty-Travis, D. C. Moule, E. C. Lim, and R. H. Judge, *The Journal of Chemical Physics* **117**, 4831 (2002).
- [143] K. Fehre, S. Eckart, M. Kunitski, M. Pitzer, S. Zeller, C. Janke, D. Trabert, J. Rist, M. Weller, A. Hartung, et al., *Science Advances* **5**, eaau7923 (2019).
- [144] in *IUPAC. Compendium of Chemical Terminology. 2nd ed. (the “Gold Book”)* (IUPAC, 2019).
- [145] D. J. D. Susan A. Zumdahl, *Chemistry* (BROOKS COLE PUB CO, 2017).
- [146] G. Wald, *Science* **162**, 230 (1968).
- [147] B. L. Feringa and W. R. Browne, eds., *Molecular Switches* (Wiley-VCH Verlag GmbH & Co. KGaA, 2011).
- [148] Z. Lu, Y. C. Chang, Q.-Z. Yin, C. Y. Ng, and W. M. Jackson, *Science* **346**, 61 (2014).
- [149] P. Pechukas, *Annual Review of Physical Chemistry* **32**, 159 (1981).

- [150] D. G. Truhlar and B. C. Garrett, Annual Review of Physical Chemistry **35**, 159 (1984).
- [151] A. G. Suits, Accounts of Chemical Research **41**, 873 (2008).
- [152] J. M. Bowman and B. C. Shepler, Annual Review of Physical Chemistry **62**, 531 (2011).
- [153] D. Townsend, S. A. Lahankar, S. K. Lee, S. D. Chambreau, A. G. Suits, X. Zhang, J. Rheinecker, L. B. Harding, and J. M. Bowman, Science **306**, 1158 (2004).
- [154] D. G. Truhlar, B. C. Garrett, and S. J. Klippenstein, The Journal of Physical Chemistry **100**, 12771 (1996).
- [155] J. L. Bao and D. G. Truhlar, Chemical Society Reviews **46**, 7548 (2017).
- [156] B. R. Heazlewood, M. J. T. Jordan, S. H. Kable, T. M. Selby, D. L. Osborn, B. C. Shepler, B. J. Braams, and J. M. Bowman, Proceedings of the National Academy of Sciences **105**, 12719 (2008).
- [157] M. L. Hause, N. Herath, R. Zhu, M. C. Lin, and A. G. Suits, Nature Chemistry **3**, 932 (2011).
- [158] M. P. Grubb, M. L. Warter, H. Xiao, S. Maeda, K. Morokuma, and S. W. North, Science **335**, 1075 (2012).
- [159] T. Endo, S. P. Neville, V. Wanie, S. Beaulieu, C. Qu, J. Deschamps, P. Lassonde, B. E. Schmidt, H. Fujise, M. Fushitani, et al., Science **370**, 1072 (2020).
- [160] V. Brites, J. Eland, and M. Hochlaf, Chemical Physics **346**, 23 (2008).
- [161] J. L. Krause, M. Shapiro, and P. Brumer, The Journal of Chemical Physics **92**, 1126 (1990).
- [162] R. J. Gordon and S. A. Rice, Annual Review of Physical Chemistry **48**, 601 (1997).
- [163] R. J. Levis and H. A. Rabitz, The Journal of Physical Chemistry A **106**, 6427 (2002).

- [164] M. Dantus and V. V. Lozovoy, Chemical Reviews **104**, 1813 (2004).
- [165] Y. Silberberg, Annual Review of Physical Chemistry **60**, 277 (2009).
- [166] K. Ohmori, Annual Review of Physical Chemistry **60**, 487 (2009).
- [167] B. Kaufman, T. Rozgonyi, P. Marquetand, and T. Weinacht, Physical Review Letters **125**, 053202 (2020).
- [168] C. P. Koch, M. Ndong, and R. Kosloff, Faraday Discussions **142**, 389 (2009).
- [169] C. P. Koch and M. Shapiro, Chemical Reviews **112**, 4928 (2012).
- [170] L. Levin, W. Skomorowski, L. Rybak, R. Kosloff, C. P. Koch, and Z. Amitay, Physical Review Letters **114**, 233003 (2015).
- [171] M. J. Wright, S. D. Gensemer, J. Vala, R. Kosloff, and P. L. Gould, Physical Review Letters **95**, 063001 (2005).
- [172] M. Viteau, A. Chotia, M. Allegrini, N. Bouloufa, O. Dulieu, D. Comparat, and P. Pillet, Science **321**, 232 (2008).
- [173] C.-Y. Lien, C. M. Seck, Y.-W. Lin, J. H. Nguyen, D. A. Tabor, and B. C. Odom, Nature Communications **5**, 4783 (2014).
- [174] J. J. García-Ripoll, P. Zoller, and J. I. Cirac, Physical Review Letters **91**, 157901 (2003).
- [175] B. Scharfenberger, W. J. Munro, and K. Nemoto, New Journal of Physics **16**, 093043 (2014).
- [176] C. Bäuerle, D. C. Glattli, T. Meunier, F. Portier, P. Roche, P. Roulleau, S. Takada, and X. Waintal, Reports on Progress in Physics **81**, 056503 (2018).
- [177] C. Uiberacker and W. Jakubetz, The Journal of Chemical Physics **120**, 11540 (2004).

- [178] K. Hoki, L. González, M. F. Shibl, and Y. Fujimura, *The Journal of Physical Chemistry A* **108**, 6455 (2004).
- [179] B. Dietzek, B. Brüggemann, T. Pascher, and A. Yartsev, *J. Am. Chem. Soc.* **129**, 13014 (2007).
- [180] A. C. Florean, D. Cardoza, J. L. White, J. K. Lanyi, R. J. Sension, and P. H. Bucksbaum, *Proceedings of the National Academy of Sciences* **106**, 10896 (2009).
- [181] C. K. Chan, P. Brumer, and M. Shapiro, *The Journal of Chemical Physics* **94**, 2688 (1991).
- [182] L. Zhu, V. Kleiman, X. Li, S. P. Lu, K. Trentelman, and R. J. Gordon, *Science* **270**, 77 (1995).
- [183] E. Charron, A. Giusti-Suzor, and F. H. Mies, *Physical Review Letters* **71**, 692 (1993).
- [184] E. Charron, A. Giusti-Suzor, and F. H. Mies, *Physical Review Letters* **75**, 2815 (1995).
- [185] B. Sheehy, B. Walker, and L. F. DiMauro, *Phys. Rev. Lett.* **74**, 4799 (1995).
- [186] D. Ray, F. He, S. De, W. Cao, H. Mashiko, P. Ranitovic, K. P. Singh, I. Znakovskaya, U. Thumm, G. G. Paulus, et al., *Physical Review Letters* **103**, 223201 (2009).
- [187] S. De, I. Znakovskaya, D. Ray, F. Anis, N. G. Johnson, I. A. Bocharova, M. Margravelidze, B. D. Esry, C. L. Cocke, I. V. Litvinyuk, et al., *Physical Review Letters* **103**, 153002 (2009).
- [188] K. J. Betsch, D. W. Pinkham, and R. R. Jones, *Physical Review Letters* **105**, 223002 (2010).
- [189] X. Gong, P. He, Q. Song, Q. Ji, H. Pan, J. Ding, F. He, H. Zeng, and J. Wu, *Physical Review Letters* **113**, 203001 (2014).

- [190] V. Wanie, H. Ibrahim, S. Beaulieu, N. Thiré, B. E. Schmidt, Y. Deng, A. S. Alnaser, I. V. Litvinyuk, X.-M. Tong, and F. Légaré, *Journal of Physics B: Atomic, Molecular and Optical Physics* **49**, 025601 (2015).
- [191] G. G. Paulus, F. Grasbon, H. Walther, P. Villoresi, M. Nisoli, S. Stagira, E. Priori, and S. D. Silvestri, *Nature* **414**, 182 (2001).
- [192] V. Roudnev, B. D. Esry, and I. Ben-Itzhak, *Physical Review Letters* **93**, 163601 (2004).
- [193] V. Roudnev and B. D. Esry, *Physical Review A* **76**, 023403 (2007).
- [194] T. M. Fortier, P. A. Roos, D. J. Jones, S. T. Cundiff, R. D. R. Bhat, and J. E. Sipe, *Physical Review Letters* **92**, 147403 (2004).
- [195] M. F. Kling, C. Siedschlag, A. J. Verhoef, J. I. Khan, M. Schultze, T. Uphues, Y. Ni, M. Uiberacker, M. Drescher, F. Krausz, et al., *Science* **312**, 246 (2006).
- [196] T. Rathje, N. G. Johnson, M. Möller, F. Süßmann, D. Adolph, M. Kübel, R. Kienberger, M. F. Kling, G. G. Paulus, and A. M. Sayler, *Journal of Physics B: Atomic, Molecular and Optical Physics* **45**, 074003 (2012).
- [197] T. Rathje, A. M. Sayler, S. Zeng, P. Wustelt, H. Figger, B. D. Esry, and G. G. Paulus, *Physical Review Letters* **111**, 093002 (2013).
- [198] N. Ishii, K. Kaneshima, K. Kitano, T. Kanai, S. Watanabe, and J. Itatani, *Nature Communications* **5**, 3331 (2014).
- [199] A. S. Alnaser and I. V. Litvinyuk, *Journal of Physics B: Atomic, Molecular and Optical Physics* **50**, 032002 (2017).
- [200] D. Goswami, *Physics Reports* **374**, 385 (2003).
- [201] A. M. Weiner, *Optics Communications* **284**, 3669 (2011).

- [202] J. McKenna, M. Zohrabi, B. Gaire, D. Ray, K. D. Carnes, D. Ursrey, J. Hernandez, F. Anis, B. D. Esry, and I. Ben-Itzhak, *Journal of Physics: Conference Series* **388**, 032045 (2012).
- [203] D. Ursrey, F. Anis, and B. D. Esry, *Physical Review A* **85**, 023429 (2012).
- [204] D. Ursrey and B. D. Esry, *Physical Review A* **96**, 063409 (2017).
- [205] P. Salières, A. L'Huillier, P. Antoine, and M. Lewenstein, in *Advances In Atomic, Molecular, and Optical Physics* (Elsevier, 1999), p. 83.
- [206] R. A. Bartels, A. Paul, H. Green, H. C. Kapteyn, M. M. Murnane, S. Backus, I. P. Christov, Y. Liu, D. Attwood, and C. Jacobsen, *Science* **297**, 376 (2002).
- [207] M. Bellini, C. Lyngå, A. Tozzi, M. B. Gaarde, T. W. Hänsch, A. L'Huillier, and C.-G. Wahlström, *Physical Review Letters* **81**, 297 (1998).
- [208] C. Benko, T. K. Allison, A. Cingöz, L. Hua, F. Labaye, D. C. Yost, and J. Ye, *Nature Photonics* **8**, 530 (2014).
- [209] C. M. Heyl, C. L. Arnold, A. Couairon, and A. L'Huillier, *Journal of Physics B: Atomic, Molecular and Optical Physics* **50**, 013001 (2017).
- [210] K. Midorikawa, *Japanese Journal of Applied Physics* **50**, 090001 (2011).
- [211] J. Li, J. Lu, A. Chew, S. Han, J. Li, Y. Wu, H. Wang, S. Ghimire, and Z. Chang, *Nature Communications* **11**, 2748 (2020).
- [212] J. Duris, S. Li, T. Driver, E. G. Champenois, J. P. MacArthur, A. A. Lutman, Z. Zhang, P. Rosenberger, J. W. Aldrich, R. Coffee, et al., *Nature Photonics* **14**, 30 (2019).
- [213] S. Baker, J. S. Robinson, C. A. Haworth, H. Teng, R. A. Smith, C. C. Chirilă, M. Lein, J. W. G. Tisch, and J. P. Marangos, *Science* **312**, 424 (2006).
- [214] T. T. Luu, Z. Yin, A. Jain, T. Gaumnitz, Y. Pertot, J. Ma, and H. J. Wörner, *Nature Communications* **9**, 3723 (2018).

- [215] Z. Yin, T. T. Luu, and H. J. Wörner, *Journal of Physics: Photonics* **2**, 044007 (2020).
- [216] S. Ghimire, A. D. DiChiara, E. Sistrunk, P. Agostini, L. F. DiMauro, and D. A. Reis, *Nature Physics* **7**, 138 (2010).
- [217] S. Ghimire and D. A. Reis, *Nature Physics* **15**, 10 (2018).
- [218] J. L. Krause, K. J. Schafer, and K. C. Kulander, *Phys. Rev. Lett.* **68**, 3535 (1992).
- [219] P. B. Corkum, *Phys. Rev. Lett.* **71**, 1994 (1993).
- [220] M. Lewenstein, P. Balcou, M. Y. Ivanov, A. L’Huillier, and P. B. Corkum, *Phys. Rev. A* **49**, 2117 (1994).
- [221] D. B. Milošević, G. G. Paulus, D. Bauer, and W. Becker, *Journal of Physics B: Atomic, Molecular and Optical Physics* **39**, R203 (2006).
- [222] W. Becker, S. P. Goreslavski, D. B. Milošević, and G. G. Paulus, *Journal of Physics B: Atomic, Molecular and Optical Physics* **51**, 162002 (2018).
- [223] M. Meckel, D. Comtois, D. Zeidler, A. Staudte, D. Pavicic, H. C. Bandulet, H. Pepin, J. C. Kieffer, R. Dorner, D. M. Villeneuve, et al., *Science* **320**, 1478 (2008).
- [224] C. I. Blaga, J. Xu, A. D. DiChiara, E. Sistrunk, K. Zhang, P. Agostini, T. A. Miller, L. F. DiMauro, and C. D. Lin, *Nature* **483**, 194 (2012).
- [225] B. Wolter, M. G. Pullen, A.-T. Le, M. Baudisch, K. Doblhoff-Dier, A. Senftleben, M. Hemmer, C. D. Schröter, J. Ullrich, T. Pfeifer, et al., *Science* **354**, 308 (2016).
- [226] E. Cormier and M. Lewenstein, *The European Physical Journal D - Atomic, Molecular, Optical and Plasma Physics* **12**, 227 (2000).
- [227] I. Kim, C. Kim, H. Kim, G. Lee, Y. Lee, J. Park, D. Cho, and C. Nam, *Phys. Rev. Lett.* **94**, 243901 (2005).
- [228] T. T. Liu, T. Kanai, T. Sekikawa, and S. Watanabe, *Phys. Rev. A* **73**, 063823 (2006).

- [229] G. Lambert, J. Gautier, C. P. Hauri, P. Zeitoun, C. Valentin, T. Marchenko, F. Tissandier, J. P. Goddet, M. Ribiere, G. Rey, et al., *New Journal of Physics* **11**, 083033 (2009).
- [230] S. Watanabe, K. Kondo, Y. Nabekawa, A. Sagisaka, and Y. Kobayashi, *Phys. Rev. Lett.* **73**, 2692 (1994).
- [231] T. Kroh, C. Jin, P. Krogen, P. D. Keathley, A.-L. Calendron, J. P. Siqueira, H. Liang, E. L. Falcão-Filho, C. D. Lin, F. X. Kärtner, et al., *Optics Express* **26**, 16955 (2018).
- [232] T. Popmintchev, M.-C. Chen, A. Bahabad, M. Gerrity, P. Sidorenko, O. Cohen, I. P. Christov, M. M. Murnane, and H. C. Kapteyn, *Proceedings of the National Academy of Sciences* **106**, 10516 (2009).
- [233] R. Boyd, *Nonlinear Optics* (Academic Press, 2008).
- [234] B. E. A. Saleh and M. C. Teich, *Fundamentals of Photonics* (Wiley, 1991).
- [235] A. D. Shiner, C. Trallero-Herrero, N. Kajumba, H.-C. Bandulet, D. Comtois, F. Légaré, M. Giguère, J.-C. Kieffer, P. B. Corkum, and D. M. Villeneuve, *Phys. Rev. Lett.* **103**, 073902 (2009).
- [236] C. Marceau, T. J. Hammond, A. Y. Naumov, P. B. Corkum, and D. M. Villeneuve, *Journal of Physics Communications* **1**, 015009 (2017).
- [237] E. Takahashi, Y. Nabekawa, and K. Midorikawa, *Opt. Lett.* **27**, 1920 (2002).
- [238] S. Hädrich, J. Rothhardt, M. Krebs, S. Demmler, A. Klenke, A. Tünnermann, and J. Limpert, *Journal of Physics B: Atomic, Molecular and Optical Physics* **49**, 172002 (2016).
- [239] I. Makos, I. Orfanos, A. Nayak, J. Peschel, B. Major, I. Lontos, E. Skantzakis, N. Papadakis, C. Kalpouzos, M. Dumergue, et al., *Scientific Reports* **10**, 3759 (2020).

- [240] Y. Tamaki, J. Itatani, Y. Nagata, M. Obara, and K. Midorikawa, *Physical Review Letters* **82**, 1422 (1999).
- [241] J. R. Sutherland, E. L. Christensen, N. D. Powers, S. E. Rhynard, J. C. Painter, and J. Peatross, *Optics Express* **12**, 4430 (2004).
- [242] P. Rudawski, C. M. Heyl, F. Brizuela, J. Schwenke, A. Persson, E. Mansten, R. Rakowski, L. Rading, F. Campi, B. Kim, et al., *Review of Scientific Instruments* **84**, 073103 (2013).
- [243] H.-W. Sun, P.-C. Huang, Y.-H. Tzeng, J.-T. Huang, C. D. Lin, C. Jin, and M.-C. Chen, *Optica* **4**, 976 (2017).
- [244] A. Rundquist, C. G. Durfee, Z. Chang, C. Herne, S. Backus, M. M. Murnane, and H. C. Kapteyn, *Science* **280**, 1412 (1998).
- [245] D. D. Hickstein, D. R. Carlson, A. Kowligy, M. Kirchner, S. R. Domingue, N. Nader, H. Timmers, A. Lind, G. G. Ycas, M. M. Murnane, et al., *Optica* **4**, 1538 (2017).
- [246] T. Siegel, R. Torres, D. J. Hoffmann, L. Brugnera, I. Procino, A. Zaïr, J. G. Underwood, E. Springate, I. C. E. Turcu, L. E. Chipperfield, et al., *Opt. Express* **18**, 6853 (2010).
- [247] C. Jin, G. Wang, H. Wei, A.-T. Le, and C. D. Lin, *Nat Commun* **5**, 4003 (2014).
- [248] S. Haessler, T. Balčiunas, G. Fan, G. Andriukaitis, A. Pugžlys, A. Baltuška, T. Witting, R. Squibb, A. Zaïr, J. W. G. Tisch, et al., *Phys. Rev. X* **4**, 021028 (2014).
- [249] M. Sayrac, A. A. Kolomenskii, J. Dong, and H. A. Schuessler, *Journal of Electron Spectroscopy and Related Phenomena* **233**, 22 (2019).
- [250] N. Ishii, A. Kosuge, T. Hayashi, T. Kanai, J. Itatani, S. Adachi, and S. Watanabe, *Opt. Express* **16**, 20876 (2008).
- [251] A. Zaïr, M. Holler, A. Guandalini, F. Schapper, J. Biegert, L. Gallmann, U. Keller, A. S. Wyatt, A. Monmayrant, I. A. Walmsley, et al., *Physical Review Letters* **100**, 143902 (2008).

- [252] L. Brugnera, D. J. Hoffmann, T. Siegel, F. Frank, A. Zaïr, J. W. G. Tisch, and J. P. Marangos, *Phys. Rev. Lett.* **107**, 153902 (2011).
- [253] S. R. Abbing, F. Campi, F. S. Sajjadian, N. Lin, P. Smorenburg, and P. M. Kraus, *Physical Review Applied* **13**, 054029 (2020).
- [254] J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pépin, J. C. Kieffer, P. B. Corkum, and D. M. Villeneuve, *Nature* **432**, 867 (2004).
- [255] B. K. McFarland, J. P. Farrell, P. H. Bucksbaum, and M. Guhr, *Science* **322**, 1232 (2008).
- [256] O. Smirnova, Y. Mairesse, S. Patchkovskii, N. Dudovich, D. Villeneuve, P. Corkum, and M. Y. Ivanov, *Nature* **460**, 972 (2009).
- [257] P. M. Kraus, B. Mignolet, D. Baykusheva, A. Rupenyan, L. Horný, E. F. Penka, G. Grassi, O. I. Tolstikhin, J. Schneider, F. Jensen, et al., *Science* **350**, 790 (2015).
- [258] M. Lein, *Journal of Physics B: Atomic, Molecular and Optical Physics* **40**, R135 (2007).
- [259] S. Haessler, J. Caillat, and P. Salières, *Journal of Physics B: Atomic, Molecular and Optical Physics* **44**, 203001 (2011).

Appendix A

Three-dimensional momentum imaging

In this appendix, we provide the imaging equations for the COLTRIMS and ion-beam imaging techniques we used throughout the thesis.

A.1 COLTRIMS Imaging

In this section, we generalize the imaging equations derived for the field-free directions in COLTRIMS described in Section 2.3.1 to the Z axis, which is parallel to the electric field. In addition, we further elaborate on how select the channels of interest.

A.1.1 TOF proportional to $\sqrt{m/q}$

In this subsection, we show that TOF of ions is proportional to their $\sqrt{m/q}$, i.e. the square root of the fragment's mass-to-charge ratio, which is commonly known for mass spectrometry based techniques [62–65].

To show that the TOF for an arbitrary ionic fragment is proportional to the $\sqrt{m/q}$, we first assume that the ion is born at rest. In our COLTRIMS, the jet propagates along the Y axis, therefore neglecting the initial center-of-mass ion momenta along the Z direction

is reasonable. In addition, we assume that the ion accelerates at a constant rate from the interaction region to the detector. Under such assumptions, the TOF equation is given by,

$$l - z_0 = \frac{1}{2}a_{jz}t_j^2, \quad (\text{A.1})$$

where $l - z_0$ is the distance from the interaction point with the laser to the detector, t_j is the true TOF of the ion of interest¹, and a_{jz} is the ion's acceleration, given by

$$a_{jz} = \frac{q_j V}{m_j d}, \quad (\text{A.2})$$

where V is the voltage placed across the spectrometer, d is the length of the spectrometer, while q_j and m_j are the fragment's charge and mass, respectively. Plugging Eq. A.2 into Eq. A.1 and solving for t_j , we get:

$$t_j = \sqrt{\frac{2(l - z_0)d}{V}} \sqrt{\frac{m_j}{q_j}} = C \sqrt{\frac{m_j}{q_j}}, \quad (\text{A.3})$$

which shows that the TOF of the fragment is proportional to $\sqrt{m/q}$ as well as derives the proportionality constant C . Fortunately, in COLTRIMS, we can use the data to calculate C using the sharp TOF peaks of the intact molecular ions. For example, in Fig. A.1 we show the fit to the intact molecular ion peaks for the OCS molecule². From this fit, we extract both the value of C as well as t_0 .

Once the proportionality constant C is determine, we can derive the acceleration a_{jz} in terms of C by plugging Eq. A.3 into Eq. A.1, resulting in:

$$a_{jz} = \frac{2(l - z_0)}{C^2} \frac{q_j}{m_j}. \quad (\text{A.4})$$

¹Recall that the true TOF is calculated by $t_j = T_j - t_0$, where T_j is the measured TOF and t_0 is a global offset mainly due to our electronics.

²Note that we also included the residual water peak and the He⁺ buffer gas.

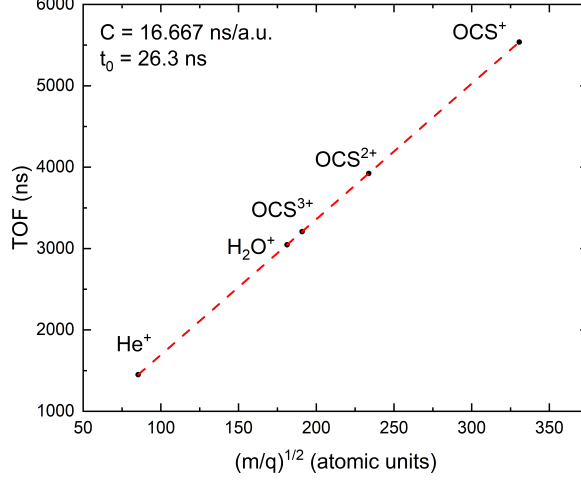


Figure A.1: The TOF as a function of $\sqrt{m/q}$ for $V = 3000$ V. The fit to the data is used to determine the values of C and t_0 .

A.1.2 Imaging equations along Z axis

Using the information above, we can derive the N-body imaging equations. Specifically, the kinematic equation for the j th fragment along the TOF dimension is given by:

$$l - z_0 = (v_{0z} - v'_{jz})t_j - \frac{1}{2}a_{jz}t_j^2 \quad (\text{A.5})$$

which is a system of N equations. In addition, momentum conservation is

$$0 = \sum_{j=1}^N m_j v'_{jz}. \quad (\text{A.6})$$

Following the same method described for the X and Y dimensions in Section 2.3.1, which are the field free directions, we then solve for v'_{jz} , resulting in

$$v'_{jz} = \frac{l - z_0}{t_j} - \frac{1}{2}a_{jz}t_j - v_{0z}. \quad (\text{A.7})$$

Next, we plug into Eq. A.6 and solve for v_{0z} , resulting in

$$v_{0z} = \frac{1}{M} \sum_{j=1}^N m_j \left(\frac{l - \bar{z}_0}{t_j} - \frac{1}{2}a_{jz}t_j \right), \quad (\text{A.8})$$

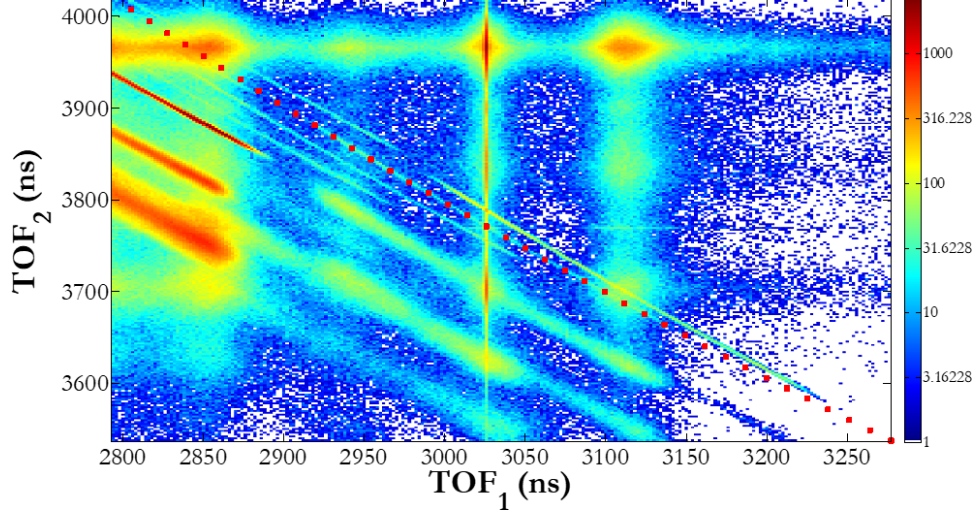


Figure A.2: *The coincidence TOF map for the two-body fragmentation of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$). The red dotted line overlays the $\text{H}_2\text{O}^+ + \text{C}_2\text{H}_4^+$ fragmentation channel.*

Recall from Section 2.3.1, we usually choose whether to solve for v_{0z} or z_0 depending on the experimental conditions. In the case of the Z dimension, the experimental contributions to the widths of v_{0z} or z_0 are about the same. In addition, the acceleration a_{jz} is also dependent on z_0 . Therefore, for consistency with the other dimensions, we chose to solve for v_{0z} in our analysis and set z_0 as an average value that is constant for all events. Finally, the momentum of the j th fragment in the center-of-mass of the recoiling molecular ion is simply given by:

$$P_{jz} = m_j v'_{jz}. \quad (\text{A.9})$$

A.1.3 Identifying and selecting coincidence channels

Generally, researchers identify ion-ion coincidence channels in COLTRIMS measurements by looking at the correlation TOF spectra of the first and second hits, which are called PIPICO (photoion-photon coincidence) or the coincidence TOF (CTOF) spectra. For example, we show a CTOF spectra in Fig. A.2 for ethanol fragmentation in a strong laser field, focusing on the $\text{H}_2\text{O}^+ + \text{C}_2\text{H}_4^+$ breakup channel. Assuming an arbitrary AB molecule that breaks into $\text{A}^+ + \text{B}^+$, such a channel appears as a sharp line at approximately 45 degrees. To select this channel, one commonly rotates the spectra by 45 degrees (by plotting the $N(t_1 + t_2, t_1 - t_2)$

spectra) and selects the channel. However, the drawback of this method is it does not generalize to three or more body breakup, which is one of our main interests throughout this thesis. Therefore, we developed a different method which does.

To simplify notation, we briefly consider the two-body breakup case. We calculate the lab frame momenta $\mathbf{p}_j$ of each fragment, i.e. we do not account for the recoiling center-of-mass of the molecular ion. We use this approach for identifying the channels because it is computationally quicker to calculate for all events in comparison to calculating the center-of-mass momenta described in the previous section. Specifically, the lab frame momenta is given by:

$$\mathbf{p}_j = m_j(\mathbf{v}_j + \mathbf{v}_0) \quad (\text{A.10})$$

Then, we know from momentum conservation that

$$M\mathbf{v}_0 = \mathbf{p}_1 + \mathbf{p}_2. \quad (\text{A.11})$$

Manipulating the equation gives

$$\mathbf{p}_2 = M\mathbf{v}_0 - \mathbf{p}_1. \quad (\text{A.12})$$

which represents a line with slope -1 and intercept $M\mathbf{v}_0$ when plotting $\mathbf{p}_2$ as a function of $\mathbf{p}_1$. Note that the line has a width due to the distribution of $M\mathbf{v}_0$. Then, we can rotate the line by simply plotting the counts as a function of the sum and difference of the momenta, i.e. $N(\mathbf{p}_1 + \mathbf{p}_2, \mathbf{p}_1 - \mathbf{p}_2)$ as shown for the Z (or TOF) axis in Fig. A.3. Then to select channels and clean the data, we set rectangular regions about the channel of interest, as shown in Fig. A.3. It is important to note that if this line is curved, it suggests there are some image distortions that need to be corrected for.

Equation A.12 can simply be generalized to N-body as

$$\sum_{i=1}^k \mathbf{p}_i = M\mathbf{v}_0 - \sum_{j=k+1}^N \mathbf{p}_j. \quad (\text{A.13})$$

Because it is arbitrary what momenta are included on the right and left sides, one can plot

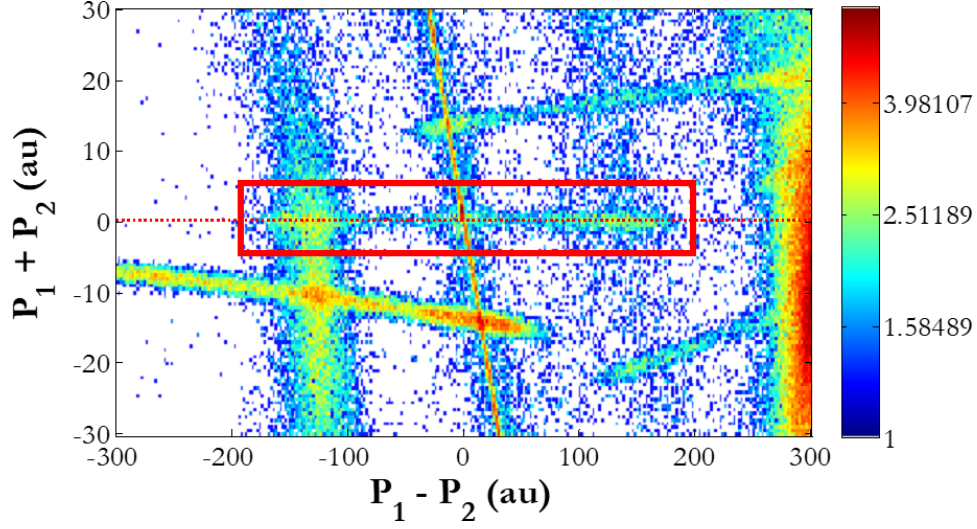


Figure A.3: Our improved method for identifying and selecting the $H_2O^+ + C_2H_4^+$ fragmentation channel using the lab frame momenta.

all the possible permutations for the difference.

A.2 Imaging molecular-ion beams

In here, we include the complete derivation of the N-body imaging equations for our ion-beam measurements conducted with the apparatus described in Section 2.4. Note that we use the same notation as previously introduced for the COLTRIMS case. Therefore, we only define the unique parameters for this case.

A.2.1 The Z-Dimension (TOF axis)

In the Z-dimension, i.e. the TOF direction, the imaging equations are given by:

$$d_1 - z_0 = (v'_{jz} + v_{0z}) t_{1j} + \frac{1}{2} a_{jz} t_{1j}^2 \quad (\text{A.14})$$

$$d_2 = v_{2j} t_{2j} = (v'_{jz} + v_{0z} + a_{jz} t_{1j}) t_{2j} \quad (\text{A.15})$$

where t_{1j} and t_{2j} are the TOFs of the j th fragment through the electric field and field free regions, respectively, and a_{jz} is the acceleration due to the spectrometer, which is given by:

$$a_{jz} = \frac{0.8Fq_jV_s}{m_jd_1} \quad (\text{A.16})$$

where F is just a calibration factor determined from Simion simulations of our system. In addition, conservation of linear momentum yields

$$0 = \sum m_j v'_{jz}, \quad (\text{A.17})$$

and we know that the true TOF (t_j) is given by

$$t_j = t_{1j} + t_{2j}. \quad (\text{A.18})$$

We then solve for v'_{jz} in Equation A.14, resulting in

$$v'_{jz} = \frac{d_1 - z_0}{t_{1j}} - \frac{1}{2}a_{jz}t_{1j} - v_{0z} \quad (\text{A.19})$$

Similarly, we solve for v_{jz} in Equation A.15, which gives us:

$$v'_{jz} = \frac{d_2}{t_{2j}} - a_{jz}t_{1j} - v_{0z} \quad (\text{A.20})$$

Solving Equation A.18 for t_{2j} and setting Equations A.19 and A.20 equal to each other, we get

$$0 = \frac{d_1 - z_0}{t_{1j}} + \frac{1}{2}a_{jz}t_{1j} - \frac{d_2}{t_j - t_{1j}}$$

If the fragment is neutral, $a_{jz} = 0$ and the solution of t_{1j} is given by:

$$t_{1j} = \frac{d_1 - z_0}{d_1 + d_2 - z_0} t_j \quad (\text{A.21})$$

On the other hand, if the fragment is charged, we then multiply through by $t_{1j}(t_j - t_{1j})$, resulting in a cubic equation in t_{1j} given by

$$0 = -\frac{1}{2}a_{jz}t_{1j}^3 + \frac{1}{2}a_{jz}t_j t_{1j}^2 + (z_0 - d_1 - d_2)t_{1j} + (d_1 - z_0)t_j = At_{1j}^3 + Bt_{1j}^2 + Ct_{1j} + D. \quad (\text{A.22})$$

which is a cubic expression in t_{1j} with an exact solution. When $a_{jz} > 0$, the only real solution is given by:

$$t_{1j} = \frac{1}{3A} \left(\frac{S}{\sqrt[3]{2}} - B - \frac{Q\sqrt[3]{2}}{S} \right) \quad (\text{A.23})$$

where Q , R , and S are given by:

$$Q = -B^2 + 3AC, \quad (\text{A.24})$$

$$R = -2B^3 + 9ABC - 27A^2D, \quad (\text{A.25})$$

$$S = \sqrt[3]{R + \sqrt{4Q^3 + R^2}}. \quad (\text{A.26})$$

On the other hand, when $a_{jz} < 0$, the relevant solution for our typical experimental conditions is

$$t_{1j} = \frac{1}{3A} \left(\frac{1 - i\sqrt{3}Q}{\sqrt[3]{4}} \frac{Q}{S} - B - \frac{1 + i\sqrt{3}}{2\sqrt[3]{2}} S \right). \quad (\text{A.27})$$

Note that there is a third possible solution to the cubic equation, however, for the experimental conditions we have run so far, it has not been the correct solution. It is important for group members to keep this fact in mind because it is possible that the relevant solutions change as different experimental conditions are explored.

The only remaining unknown to solve for is v_{0z} , which can be solved by plugging Equation A.19 into the momentum conservation condition given by Equation A.17, resulting in

$$v_{0z} = \frac{1}{M} \sum_{j=1}^N m_j \left(\frac{d_1 - z_0}{t_{1j}} - \frac{1}{2}a_{jz}t_{1j} \right). \quad (\text{A.28})$$

Then, the z component of the momentum of the j th fragment is simply given by

$$P_{jz} = m_j v'_{jz}. \quad (\text{A.29})$$

A.2.2 The X-Dimension (Deflector axis)

In the X-dimension, we include an imaging deflector that we use for measuring low KER and mass asymmetric breakup channels. The main assumption for the deflector is that it has a uniform electric field over a finite length L , where we neglect fringe fields that were minimized by using "frames" (see Refs. [39, 40] for more information).

The imaging equations for the X dimension are given by:

$$x_j - x_{dj} - M_{bfj}x_0 = (v'_{jx} + v_{0x}) M_{vj}t_j \quad (\text{A.30})$$

$$\sum_j m_j v'_{jx} = 0 \quad (\text{A.31})$$

where M_{bfj} and M_{vj} are the position and velocity magnification factors, respectively. The magnification factors are due to the diverging electric fields at the exit of the spectrometer and are determined by running Simion. x_{dj} is the amount of deflection caused by the transverse electric field of the deflector and is derived below. We then solve for the initial velocity of the fragment, given by:

$$v'_{jx} = \frac{x_j - x_{dj} - M_{bfj}x_0}{M_{vj}t_j} - v_{0x}, \quad (\text{A.32})$$

which is then substituted into the momentum conservation condition given in Equation A.31, leading to:

$$0 = \sum_j m_j \frac{x_j - x_{dj}}{M_{vj}t_j} - x_0 \sum_j \frac{m_j M_{bfj}}{M_{vj}t_j} - M v_{0x}, \quad (\text{A.33})$$

from which x_0 or v_{0x} can be solved. Both solutions are given below

$$x_0 = \left(\sum_j m_j \frac{x_j - x_{dj}}{M_{vj} t_j} - \mathcal{M} v_{0x} \right) \left(\sum_j \frac{m_j M_{bfj}}{M_{vj} t_j} \right)^{-1} \quad (\text{A.34})$$

$$v_{0x} = \frac{1}{M} \sum_j m_j \frac{x_j - x_{dj} - M_{bfj} x_0}{M_{vj} t_j}, \quad (\text{A.35})$$

though they cannot be used for the same event as was the case in COLTRIMS.

Now, we must determine the value of x_{dj} . The total amount of X deflection at the detector of the j th fragment has two contributions: (1) deflection in the deflector itself and (2) the deflection due to the increased velocity in the x-direction gained by the deflector. The two contributions add up to

$$x_{dj} = \frac{1}{2} a_{xj} t_{dj}^2 + \frac{a_{xj} t_{dj}}{v_{2jz}} l, \quad (\text{A.36})$$

where t_{dj} is just the time the fragment spends in the deflector, which is given by:

$$t_{dj} = \frac{L}{v_{2jz}}, \quad (\text{A.37})$$

where L is the length of the deflector and v_{2jz} is the fragment's drift velocity in the z direction given in Equation A.15. The acceleration due to the deflector is given by:

$$a_{xj} = \frac{q_j V_d}{D m_j}, \quad (\text{A.38})$$

where V_d is the voltage applied across the deflector and D is the distance between the deflector plates. Then, the x component of the j th fragment is simply given by:

$$P_{jx} = m_j v'_{jx}. \quad (\text{A.39})$$

The imaging in the Y dimension follows similar imaging equations as the X-dimension, except the deflector term y_{dj} is always 0.

Appendix B

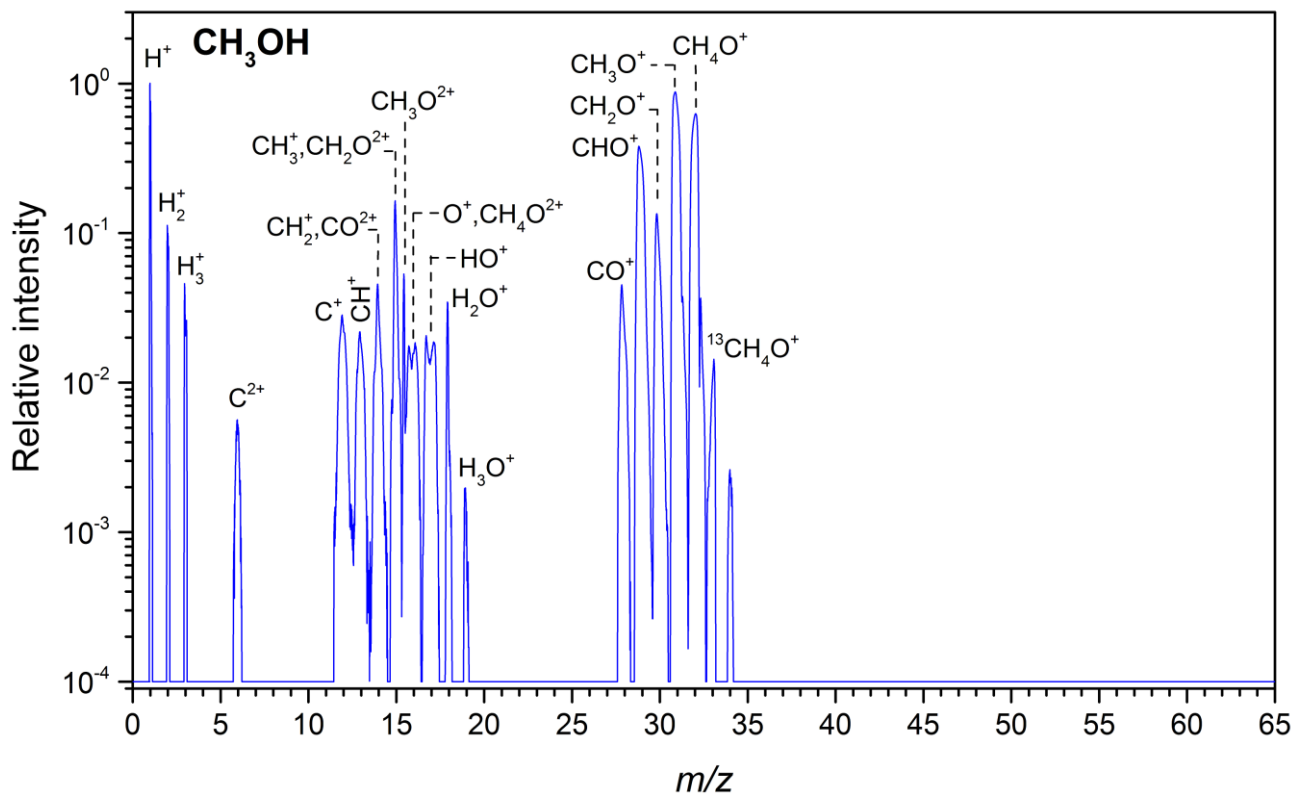
Supplementary material for H₂ roaming manuscript

Below, we include the published supplementary material for our published manuscript presented in Section [4.3](#).

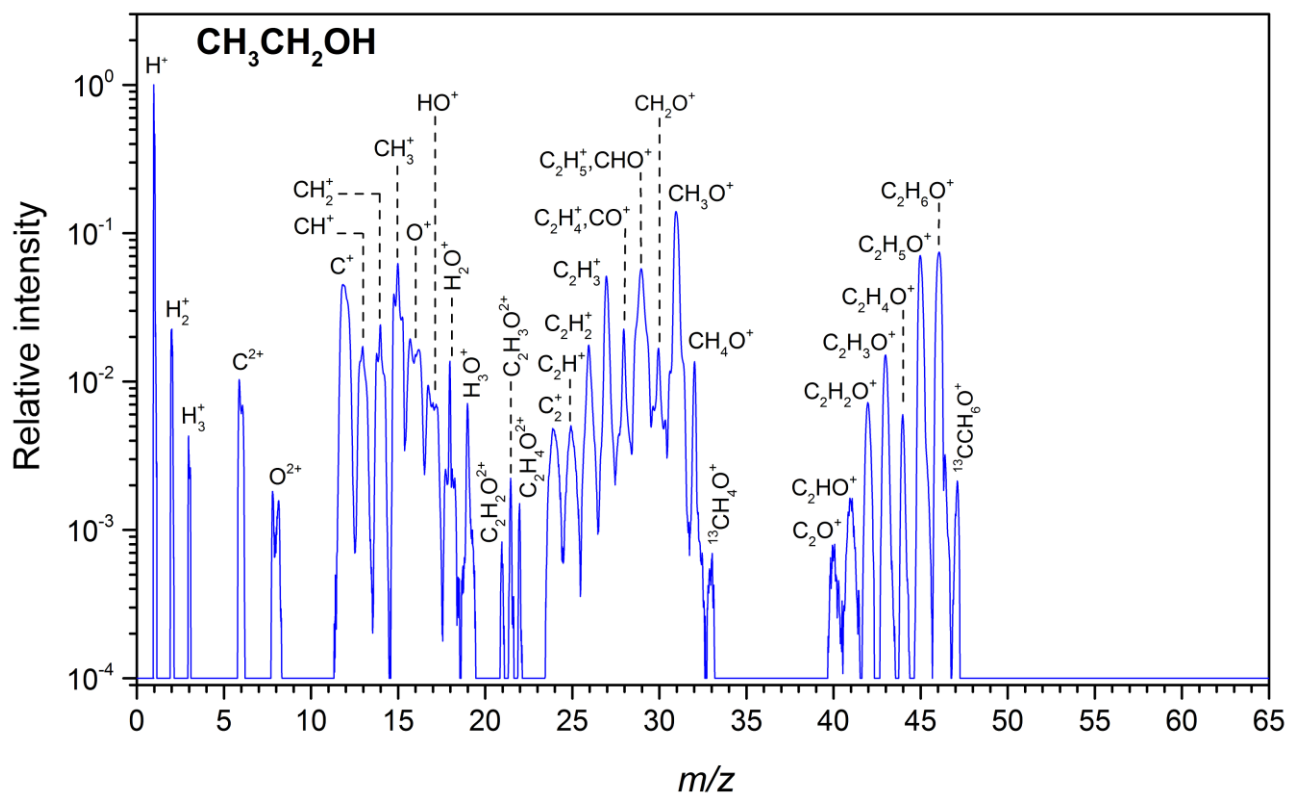
Supplementary Information

H₂ roaming chemistry and the formation of H₃⁺ from
organic molecules in strong laser fields

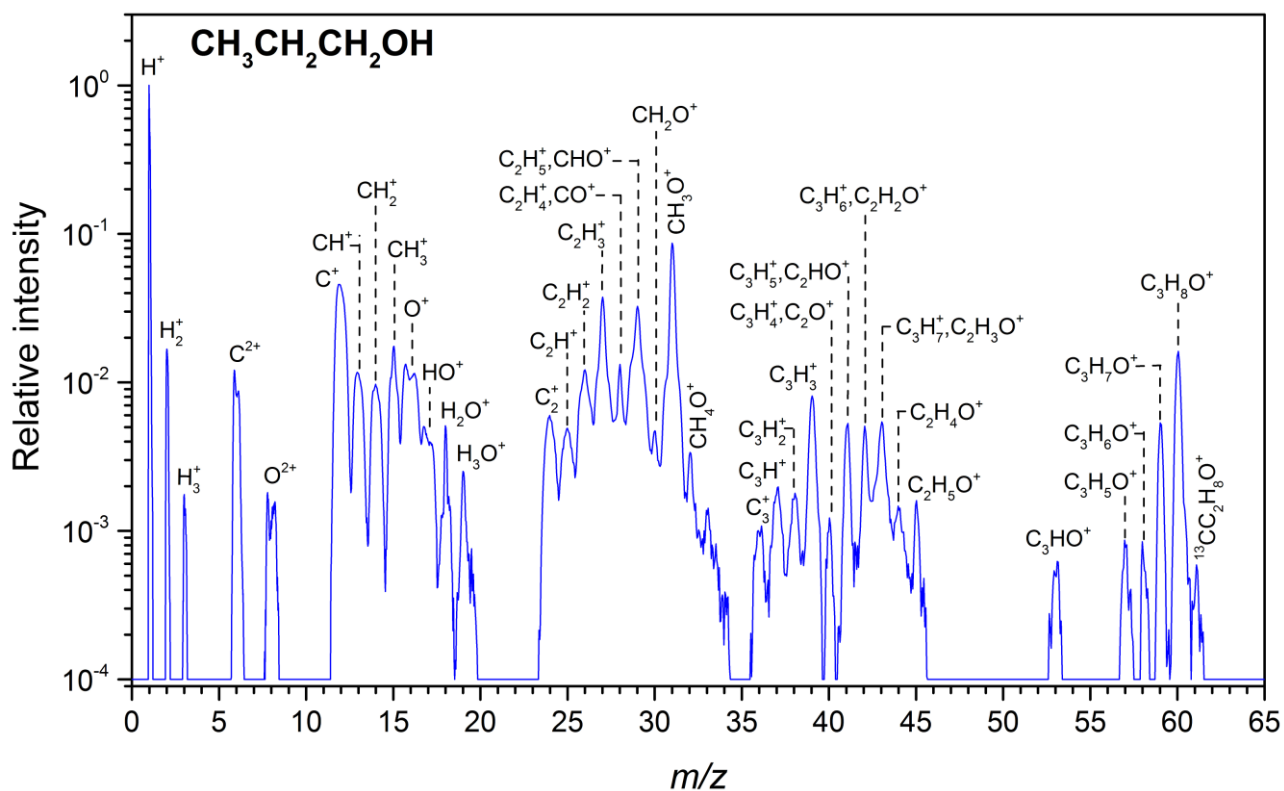
Ekanayake *et al.*



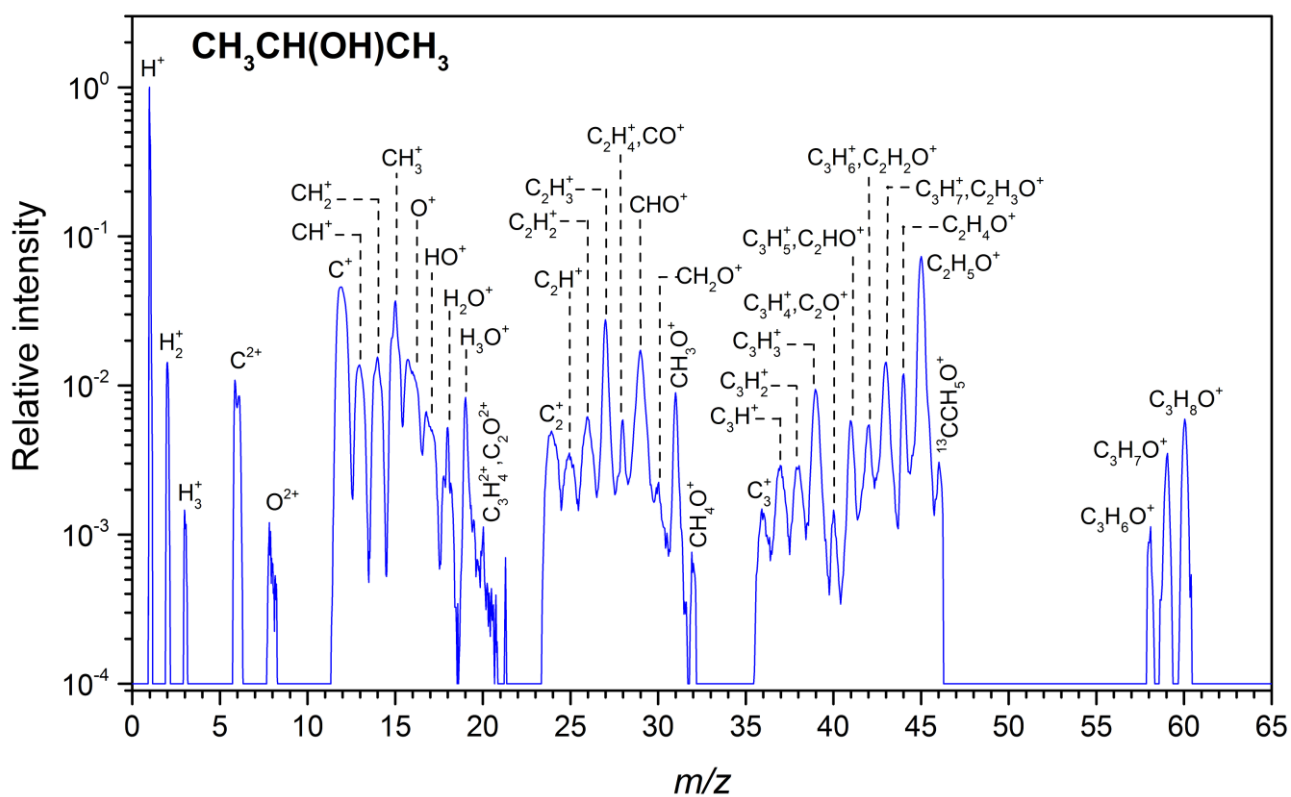
Supplementary Figure 1. CH₃OH mass-spectrum. Time-of-flight mass spectrum for dissociative ionization of dehydrated CH₃OH (methanol) in a linearly polarized laser focus of $2.0 \times 10^{14} \text{ W cm}^{-2}$. Note that in the mass spectrum, no C³⁺ yield at $m/z = 4$ was observed.



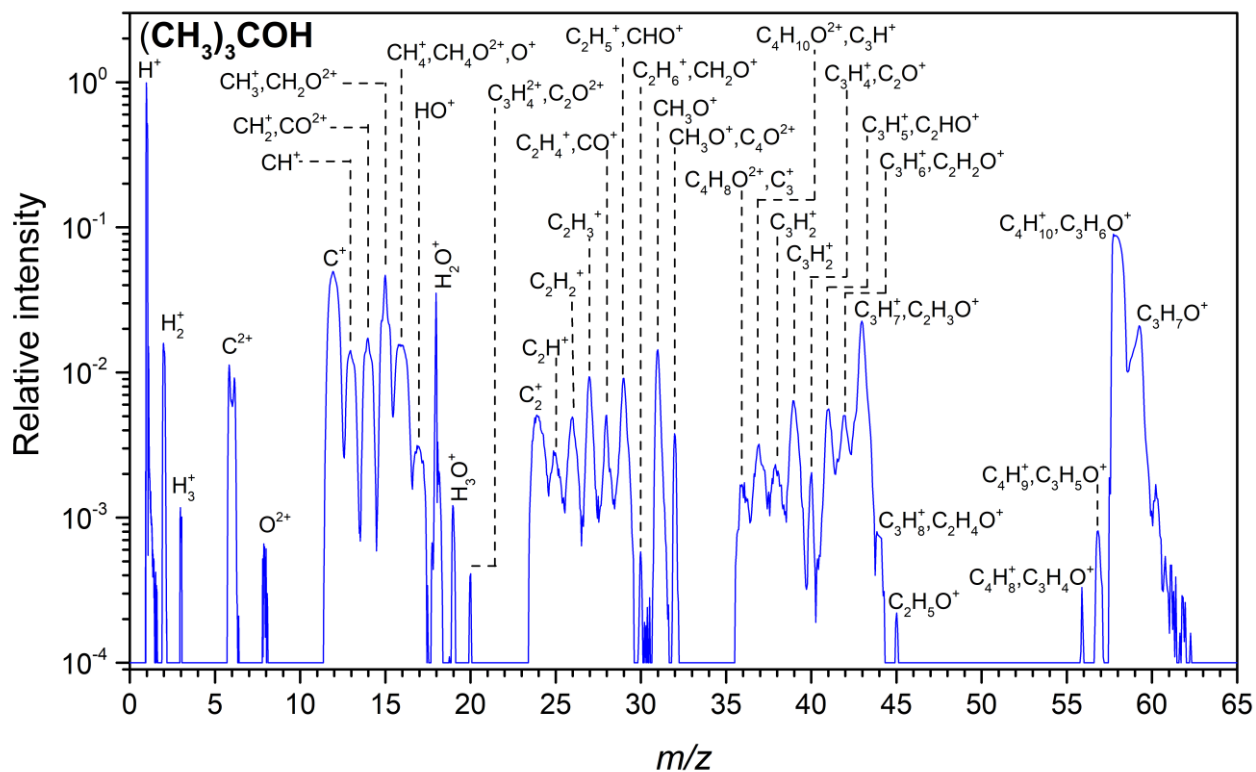
Supplementary Figure 2. CH₃CH₂OH mass spectrum. Time-of-flight mass spectrum for dissociative ionization of dehydrated CH₃CH₂OH (ethanol) in a linearly polarized laser focus of $2.0 \times 10^{14} \text{ W cm}^{-2}$. Note that in the mass spectrum, no C³⁺ yield at $m/z = 4$ was observed.



Supplementary Figure 3. CH₃CH₂CH₂OH mass spectrum. Time-of-flight mass spectrum for dissociative ionization of dehydrated CH₃CH₂CH₂OH (1-propanol) in a linearly polarized laser focus of $2.0 \times 10^{14} \text{ W cm}^{-2}$. Note that in the mass spectrum, no C^{3+} yield at $m/z = 4$ was observed.



Supplementary Figure 4. CH₃CH(OH)CH₃ mass spectrum. Time-of-flight mass spectrum for dissociative ionization of dehydrated CH₃CH(OH)CH₃ (2-propanol) in a linearly polarized laser focus of $2.0 \times 10^{14} \text{ W cm}^{-2}$. Note that in the mass spectrum, no C³⁺ yield at $m/z = 4$ was observed.



Supplementary Figure 5. (CH₃)₃COH mass spectrum. Time-of-flight mass spectrum for dissociative ionization of dehydrated (CH₃)₃COH (*tert*-butanol) in a linearly polarized laser focus of $2.0 \times 10^{14} \text{ W cm}^{-2}$. Note that in the mass spectrum, no C^{3+} yield at $m/z = 4$ was observed. No prominent ion peaks beyond $m/z = 65$ were observed except a peak at $m/z = 68$ with a relative intensity of $\sim 10^{-3}$.

Supplementary Note 1 – Normalization of TOF and CTOF data for H_3^+ production

Here we describe methods for normalizing measurements of different molecules in order to compare the production rate of a specific product – H_3^+ from alcohol molecules in our case.

Interactions causing single and double ionization of target molecules produce single ions $S_q(i)$ and ion pairs $C_q(i, j)$, where q is the number of electrons ionized. The ions are usually distinguished by their m/q , but for simplicity we use integer labeling of the peaks in the TOF spectrum. Note that single ions, specifically dications, can be produced following double ionization – we include the cation and dication parent molecule among the single ions.

It is common to define the fragmentation pattern, or the branching ratios of each parent ion, as the fraction of a specific ion, or ion pair, relative to the sum of all ions originating from the same parent molecular ion. For single ionization, denoted by the subscript 1,

$$F_1(i) = \frac{S_1(i)}{\sum_k S_1(k)}. \quad (1)$$

Similarly, the branching ratios in the case of double ionization (denoted by the subscript 2) are given by

$$F_2(i) = \frac{S_2(i)}{\sum_l S_2(l) + \sum_{k \leq j} C_2(k, j)},$$

for dications, and

$$F_2(i, j) = \frac{C_2(i, j)}{\sum_l S_2(l) + \sum_{k \leq j} C_2(k, j)}, \quad (2)$$

for ion pairs.

Note that the denominator in Eq. (1) and Eq. (2) is the total number of singly or doubly-ionized parent molecules, respectively.

To simplify the problem, we assume that triple ionization is negligible, a fact that can be verified from the data. Moreover, it is helpful to focus on a specific example, so we choose the total H_3^+ production as our test case. For this fragment the equations above reduce to a single equation as the coincidence data suggests that H_3^+ is formed (predominantly) from the parent dication in ion-pair

breakup channels, i.e. $H_3^+ + m_x^+ + m_r$ [where $m_r = m - (3 + m_x)$], therefore $S_1(3) = 0$ and $S_2(3) = 0$. Then, we can write the total H_3^+ production branching ratio as

$$F_T(3) = \sum_j F_2(3, j) = \frac{\sum_j C_2(3, j)}{\sum_l S_2(l) + \sum_{k \leq j} C_2(k, j)}, \quad (3)$$

where $F_T(3)$ is defined by summing all the branching ratios of the relevant ion-pair channels. Our goal is to evaluate $F_T(3)$ for one molecule and compare it with the value determined for another molecule.

Next we consider the measured number of single ions $M(i)$ and ion-pairs $M(i, j)$ out of the total number of single ions $S(i)$ and ion-pairs $C(i, j)$ produced by the interaction. These quantities are related by a set of coupled equations that can be written as

$$M(i) = \varepsilon_i S_1(i) + \varepsilon_i S_2(i) + \varepsilon_i \sum_j C_2(i, j), \quad (4)$$

where ε_i is the detection efficiency of the i^{th} fragment, the first and second terms are single ions from single and double ionization, respectively, and the third term is due to fragments from ion pairs (i.e. the detection of either both ions without preserving their coincidence information or only one ion out of the pair caused by the less than unity detection efficiency). Similarly, the measured number of ion-ion coincidences is given by

$$M(i, j) = \varepsilon_i \varepsilon_j C_2(i, j) + \tau \varepsilon_i \varepsilon_j [S_1(i) + S_2(i)][S_1(j) + S_2(j)], \quad (5)$$

where the first term is due to true ion-pairs, while the second is due to random (also known as “false”) coincidences associated with the random-coincidence rate coefficient, τ . Random-coincidence events can be also due to a single ion and an ion-pair, two ion pairs, etc. produced in the same pulse. These higher order contributions are much less likely and for simplicity they are not shown in Eq. (5), however, they are all subtracted by our random-pair subtraction algorithm. These random coincidences can be subtracted from Eq. (5) before proceeding. To that end, we generate a large set of purely random ion-pairs by pairing ions generated in different laser pulses (taking advantage of the data recorded event by event). That data set is scaled to the measured data using a purely random

coincidence ion pair, for example $\text{CH}_3\text{OH}^+ + \text{OH}^+$ coincidences in methanol, and then subtracted (see, sub section iii.). Using the resulting “random-coincidence free” spectra we evaluate

$$M'(i, j) = \varepsilon_i \varepsilon_j C_2(i, j). \quad (6)$$

For our example, H_3^+ production, Eqs. (4) and (6) simplify to

$$M(3) \approx \varepsilon_3 \sum_j C_2(3, j), \quad (7)$$

$$M'(3, j) \approx \varepsilon_3 \varepsilon_j C_2(3, j), \quad (8)$$

as we can neglect the $S_1(3)$ [see, our recent work¹ where we used the high KER of the H_3^+ fragment to exclude breakup from the cation] and the $S_2(3)$ terms. Assuming the same detection efficiency for all ions the equations above simplify further to

$$M(3) \approx \varepsilon \sum_j C_2(3, j), \quad (9)$$

$$M'(3, j) \approx \varepsilon^2 C_2(3, j). \quad (10)$$

i. TOF normalization

Now, we define the normalized yield of H_3^+ , also called the “fractional H_3^+ yield” in the main paper, as the ratio of the measured number of H_3^+ ions and the sum over all ions measured in a TOF spectrum, that is

$$\frac{M(3)}{\sum_k M(k)} \approx \frac{\varepsilon \sum_j C_2(3, j)}{\varepsilon \sum_m S_1(m) + \varepsilon \sum_l S_2(l) + \varepsilon \sum_{k \leq j} C_2(k, j)}, \quad (11)$$

which simplifies to

$$\frac{M(3)}{\sum_i M(i)} \approx \frac{\sum_j C_2(3, j)}{\sum_m S_1(m) + \sum_l S_2(l) + \sum_{k \leq j} C_2(k, j)}. \quad (12)$$

Recall that the number of ions produced by photo-ionization (or a similar linear process) can be written as

$$S_1(m) = \int_0^t y_1(m) dt = \int_0^t \sigma_1 F_1(m) N_T n_p dt, \quad (13)$$

where σ_1 is the single ionization cross section, $F_1(m)$ is the fraction of a specific ion produced by single ionization, N_T is the target number density and n_p is the number of photons per second. It is important to note that $\sum_m F_1(m) = 1$ and $\sum_l F_2(l) + \sum_{k \leq j} F_2(k, j) = 1$.

Assuming that the target density is not fluctuating too much, the expression above can be simplified to

$$S_1(m) = \sigma_1 F_1(m) \overline{N_T} \int_0^t n_p dt = \sigma_1 F_1(m) \overline{N_T} N_p, \quad (14)$$

where $\overline{N_T}$ is the average target density, and N_p is the total number of photons in the measurement. A similar expression can be written for the double ionization leading either to single ions, i.e. $A^{2+} + B$, or an $A^+ + B^+$ ion pair.

Substituting the equation above (and the similar equation for double ionization) in Eq. (12) yields

$$\frac{M(3)}{\sum_k M(k)} \simeq \frac{\sum_j \sigma_2 F_2(3, j) \overline{N_T} N_p}{\sum_m \sigma_1 F_1(m) \overline{N_T} N_p + \sum_l \sigma_2 F_2(l) \overline{N_T} N_p + \sum_{k \leq j} \sigma_2 F_2(k, j) \overline{N_T} N_p}. \quad (15)$$

Note that, as expected, the target density and the number of photons (or the number of laser pulses) cancel out, however, the single and double photoionization cross sections do not. Dividing the numerator and denominator in the equation above by σ_2 yields

$$\frac{M(3)}{\sum_k M(k)} \simeq \frac{\sum_j F_2(3, j)}{\frac{\sigma_1}{\sigma_2} \sum_m F_1(m) + \sum_l F_2(l) + \sum_{k \leq j} F_2(k, j)}, \quad (16)$$

which can be further simplified to

$$\frac{M(3)}{\sum_k M(k)} \simeq \frac{\sum_j F_2(3, j)}{\frac{\sigma_1}{\sigma_2} + 1}. \quad (17)$$

by using $\sum_m F_1(m) = 1$ and $\sum_l F_2(l) + \sum_{k,j} F_2(k, j) = 1$.

It is important to note that comparing the H_3^+ production between two molecules using the normalization procedure detailed above yields

$$\frac{M(3) / \sum_k M(k)}{M''(3) / \sum_{k''} M''(k'')} \approx \frac{\left(\frac{\sigma_1''+1}{\sigma_2''}\right) \sum_j F_2(3, j)}{\left(\frac{\sigma_1+1}{\sigma_2}\right) \sum_{j''} F_2''(3, j'')}, \quad (18)$$

and not the desired $\sum_j F_2(3, j) / \sum_j F_2''(3, j)$ ratio.

Note that σ_1 / σ_2 can be a very large number because it is much easier to ionize one electron than two. More importantly, σ_1 and σ_2 typically differ significantly from one molecule to another, especially in a strong field for which ionization is known to depend strongly on I_p – and I_p is different for the alcohols we have studied². Therefore, this normalization approach may not accurately provide the desired ratio needed in order to compare between molecules. Moreover, the assumption that H_3^+ is not a product of the cation may not be valid for all molecules.

ii. CTOF normalization

To circumvent the issue with the normalization method described above, we employ coincidence time-of-flight (CTOF) and define the total H_3^+ branching ratio as the ratio between the sum of the $H_3^+ + m_x^+$ ion pairs produced and the sum over all events involving the parent dication molecule, that is

$$F_T(3) \equiv \frac{\sum_j C_2(3, j)}{\sum_l S_2(l) + \sum_{k \leq j} C_2(k, j)}. \quad (19)$$

Here, we need to determine *first* the number of ion-pairs produced, $C_2(k, j)$ after subtraction of the random coincidences using Eq. (6), which can be rewritten as

$$C_2(k, j) = \frac{1}{\epsilon^2} M'(k, j). \quad (20)$$

assuming the same detection efficiency, ϵ , for all ions. Similarly the few $A^{2+} + B$ and AB^{2+} yields, $S_2(i)$, need to be determined by using Eq. (4), which can be rewritten as

$$S_2(i) = \frac{1}{\varepsilon} M_2(i), \quad (21)$$

assuming no overlap with singly charged fragment ions in TOF, i.e. no $S_1(i)$ contribution to the specific peak of interest. Note that there are no “lost-fragments” contributions^{3,4} as we neglected triple ionization and higher. The evaluation of $S_2(i)$ and $C_2(i, j)$ may require solving the set of coupled Eqs. (4) and (5) if the simplifications above do not hold. Once $S_2(i)$ and $C_2(i, j)$ are known, the normalized yield of H_3^+ defined as

$$F_T(3) \equiv \frac{\sum_j C_2(3, j)}{\sum_l S_2(l) + \sum_{k \leq j} C_2(k, j)}, \quad (22)$$

can be related to the branching ratios by substituting Eq. (14) into the expression above, leading to

$$F_T(3) = \frac{\sum_j \sigma_2 F_2(3, j) \overline{N_T} N_p}{\sum_l \sigma_2 F_2(l) \overline{N_T} N_p + \sum_{k \leq j} \sigma_2 F_2(k, j) \overline{N_T} N_p}, \quad (23)$$

which simplifies to

$$F_T(3) = \frac{\sum_j F_2(3, j)}{\sum_l F_2(l) + \sum_{k \leq j} F_2(k, j)}, \quad (24)$$

as the average target density, $\overline{N_T}$, integrated number of photons, N_p , as well as the double ionization cross section, σ_2 , cancel out. Finally, taking advantage of $\sum_l F_2(l) + \sum_{k \leq j} F_2(k, j) = 1$ the expression above reduces to the desired normalized branching ratio,

$$F_T(3) = \sum_j F_2(3, j), \quad (25)$$

which can be compared to other molecules. Explicitly, the total H_3^+ production branching ratio can be directly compared for two molecules

$$\frac{F_T(3)}{F_T''(3)} = \frac{\sum_j F_2(3, j)}{\sum_{j''} F_2''(3, j'')}, \quad (26)$$

but we have to keep in mind that *first* we have to evaluate all $S_2(i)$ and $C_2(i, j)$ either by solving the coupled Eqs. (4) and (5), or by subtracting the random coincidences first and taking advantage of the fact that the doubly-charged dications in our case do not overlap singly charged ions.

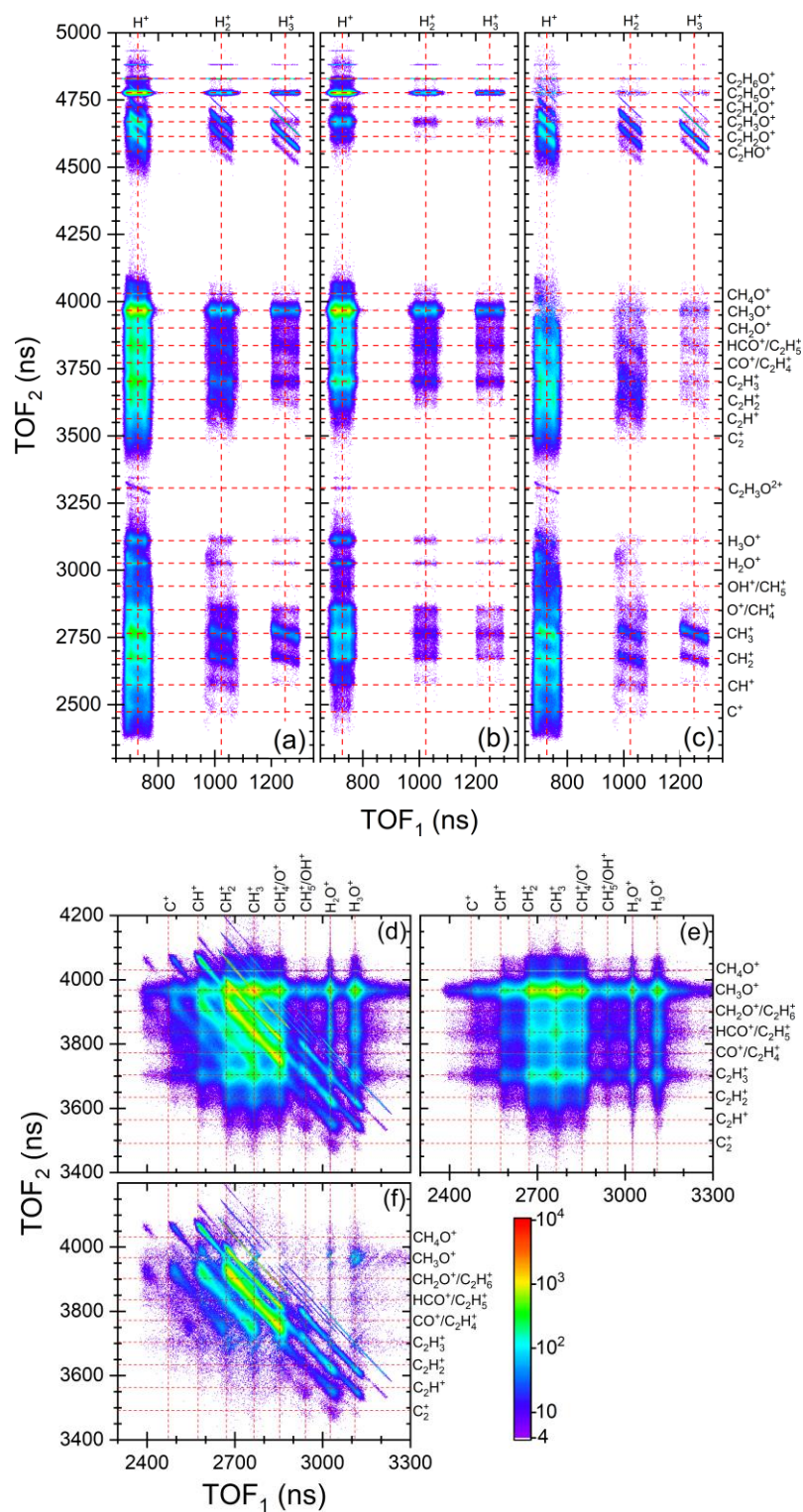
Finally, using Eqs. (3), (20), and (21), the explicit expression for the total H_3^+ production branching ratio as a function of the measured yields is given by

$$F_T(3) = \sum_j F_2(3, j) = \frac{\sum_j M'(3, j)}{\varepsilon \sum_l M_2(l) + \sum_{k \leq j} M'(k, j)}. \quad (27)$$

iii. Evaluating true coincidence events of ion pairs

The CTOF ion-pair spectra consist of both true and random (also referred to as false) coincidences. The random coincidences are due to the accidental detection of two ions from different molecules produced in the same laser pulse and pass all the conditions we impose on our ion pairs. The main source of these random events are two ions produced by single ionization, as those have a higher rate.

The spectrum of the random coincidences can be generated by pairing ions recorded for different laser pulses in our data set, which is recorded event-by-event. In Supplementary Fig. 6 we show an example of the raw CTOF data of ethanol together with the respective random coincidences scaled to match, for example the purely random $H_3O^+ + CH_3O^+$ coincidence peak. The true coincidence spectra are generated by subtracting the scaled random coincidence spectra from the raw spectra and are shown in panels (c) and (f).



Supplementary Figure 6. Coincidence time-of-flight spectra of ethanol. The raw data are shown in panels (a) and (d) for smaller and larger m/q first hits, respectively. Panels (b) and (e) show the respective random coincidences generated from the same data set (see text). The respective true coincidence spectra are shown in panels (c) and (f).

Supplementary Note 2 – TOF and CTOF analysis for H_3^+ production

i. CTOF and TOF comparison

Supplementary Table 1. Data corresponding to total H_3^+ branching ratios (CTOF) and H_3^+ production (TOF) shown in Fig. 2. The TOF data was normalized to match the CTOF branching ratio for methanol.

Molecule	H_3^+ branching ratio	$[\text{H}_3^+]$	$[\text{H}_3^+]/[\text{all ions}]$
methanol	0.142 ± 0.014	0.142 ± 0.016	0.142 ± 0.017
ethanol	0.0288 ± 0.0029	0.044 ± 0.005	0.051 ± 0.006
1-propanol	$0.00250^{+0.00250}_{-0.00027}$	0.024 ± 0.003	0.023 ± 0.003
2-propanol	Not measured	0.021 ± 0.002	0.020 ± 0.002
<i>tert</i> -butanol	Not measured	0.019 ± 0.002	0.015 ± 0.002

The errors for H_3^+ branching ratios are detailed in the next sub section. The errors indicated for $[\text{H}_3^+]$ yield include both systematic and statistical errors. Errors for $[\text{H}_3^+]/[\text{all ions}]$ are calculated through error propagation.

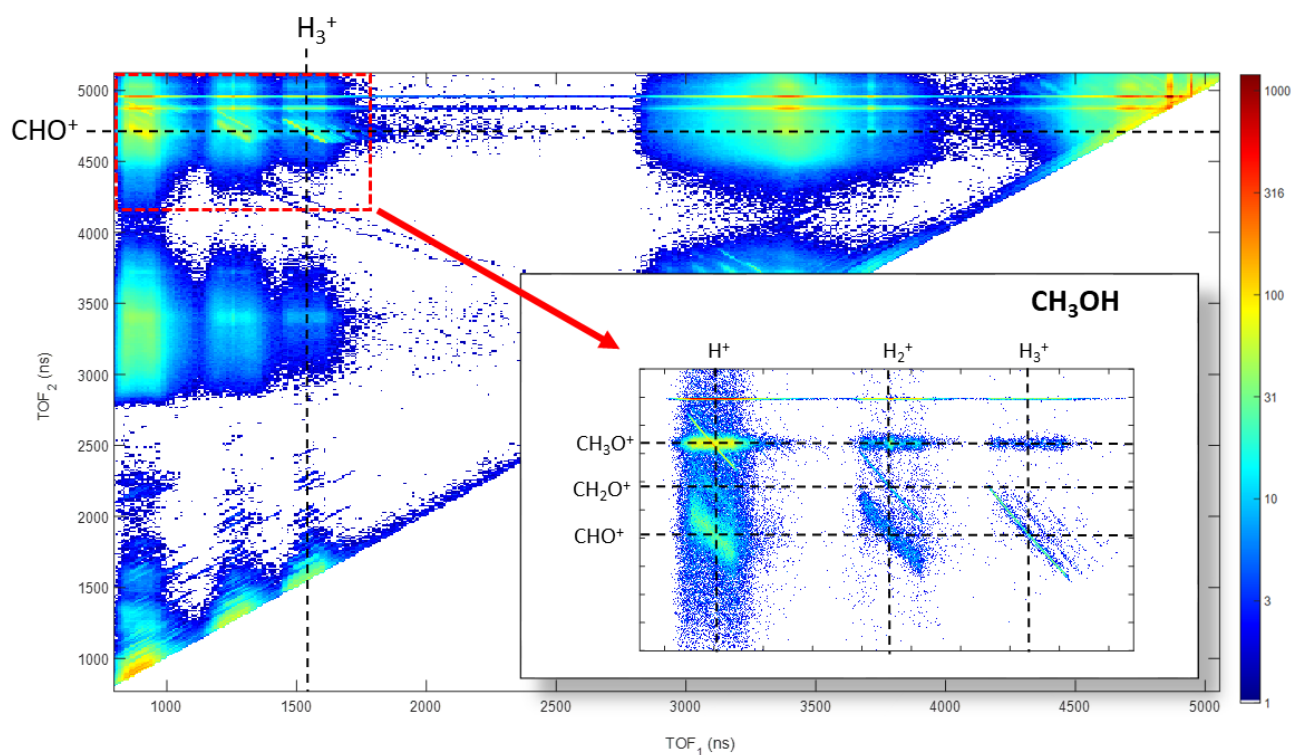
ii. CTOF branching ratios

As discussed in Supplementary Note 1, to compare the total H_3^+ production rate we need to evaluate the branching ratio of H_3^+ production as well as many other breakup channels of the dication. In addition, we need to determine the detection efficiency so that the $\text{AB}^{2+} + \text{N}$ breakup can be added to $\text{AB}^+ + \text{CD}^+ + \text{N}$ channels (where N denotes neutral fragments), as their detection efficiencies are different (ϵ for the former and ϵ^2 for the latter, assuming the same detection efficiency for all ions).

The detection efficiency was determined using the methanol and ethanol CTOF measurements, for which the H_3^+ production from the monocation is negligible (as suggested by the kinetic-energy distribution of these fragments)¹.

The errors in the branching ratios include statistical errors, errors due to subtraction of random pairs (i.e. false coincidences), and the estimated error due to losses and scaling of the generated random events.

Methanol (CH₃OH)



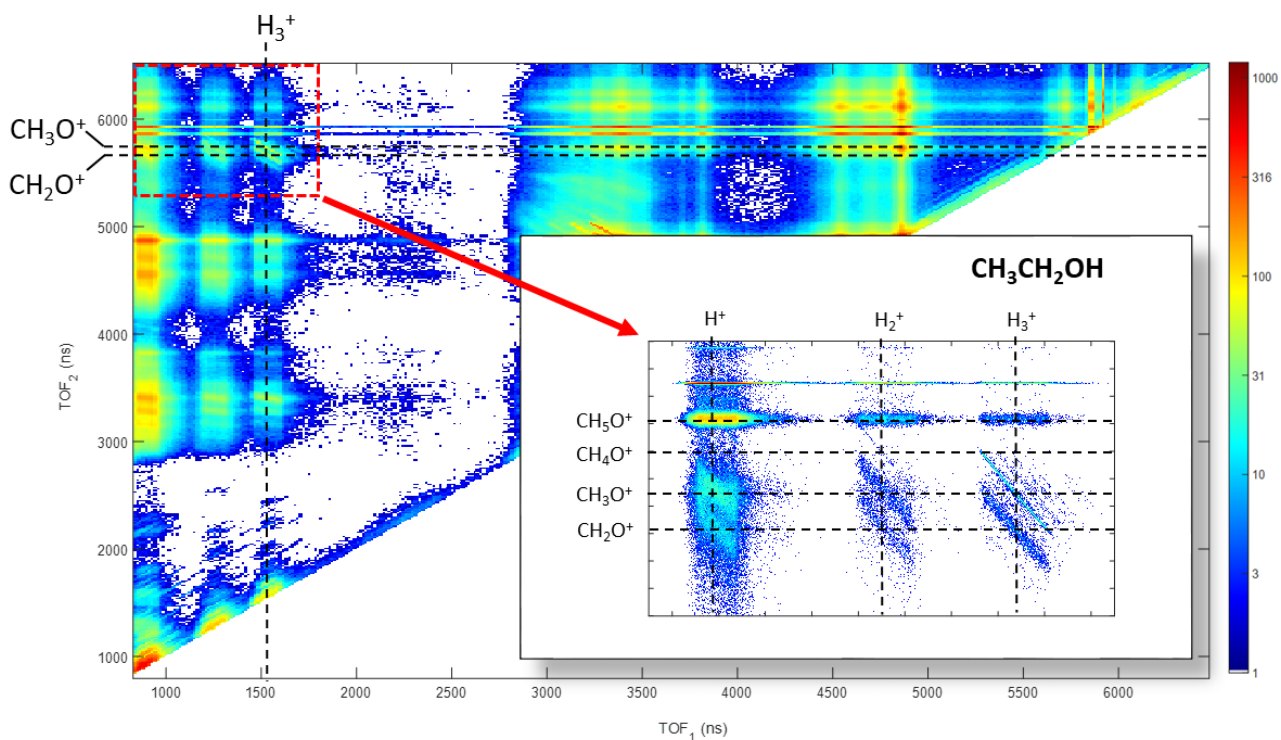
Supplementary Figure 7. Truncated coincidence time-of-flight spectrum of methanol. The CTOF spectrum from dissociative ionization of methanol in a linearly polarized laser focus of $2.0 \times 10^{14} \text{ W cm}^{-2}$. The magnified view of H^+ , H_2^+ , and H_3^+ formation channels is given in the inset. The logarithmic color scale indicates the number of events recorded.

Detection efficiency: $\varepsilon = 0.278 \pm 0.028$

Branching ratios:

$\text{H}_3^+ + \text{CHO}^+ \quad 0.142 \pm 0.014$

Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$)



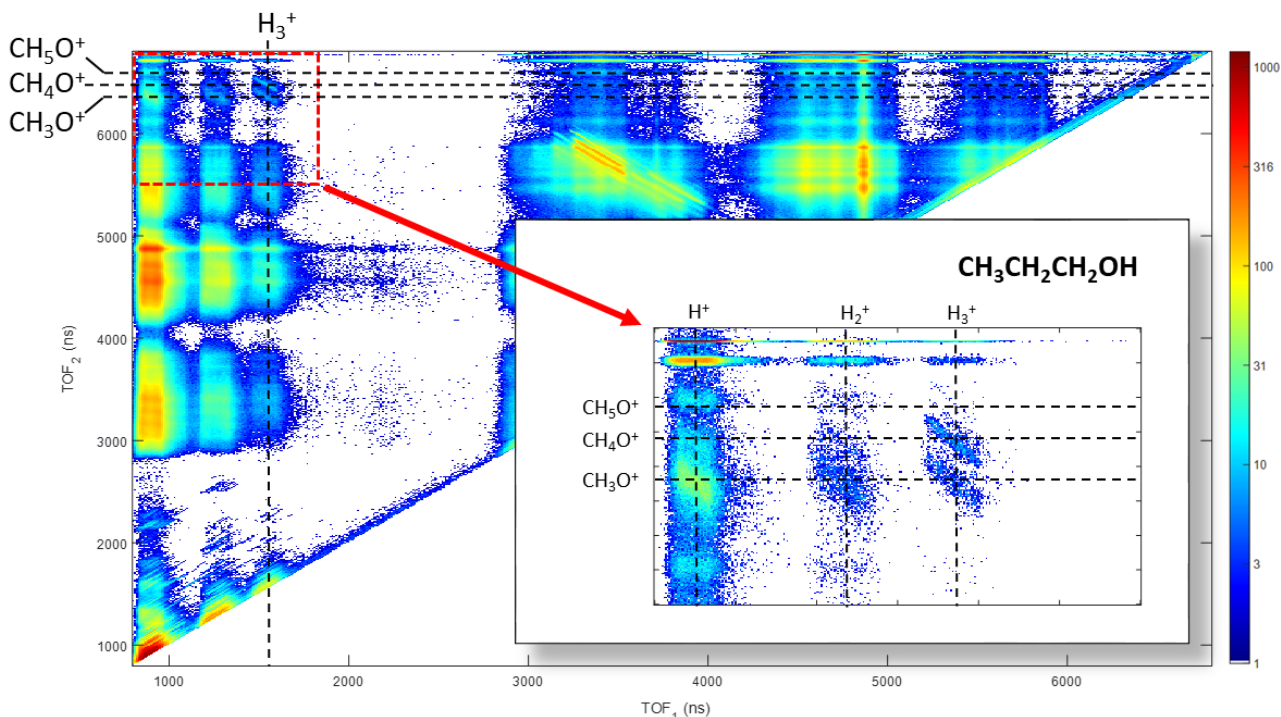
Supplementary Figure 8. Truncated coincidence time-of-flight spectrum of ethanol. The CTOF spectrum from dissociative ionization of ethanol in a linearly polarized laser focus of $2.0 \times 10^{14} \text{ W cm}^{-2}$. The magnified view of H^+ , H_2^+ , and H_3^+ formation channels is given in the inset. The logarithmic color scale indicates the number of events recorded.

Detection efficiency: $\varepsilon = 0.230 \pm 0.023$

Branching ratios:

Sum of H_3^+ channels	0.0288 ± 0.0029	
$\text{H}_3^+ + \text{CH}_3^+ + \text{CO}$	0.0108	± 0.0011
$\text{H}_3^+ + \text{C}_2\text{H}_3\text{O}^+$	0.00784	± 0.00079
$\text{H}_3^+ + \text{C}_2\text{H}_2\text{O}^+ + \text{H}$	0.00633	± 0.00064
$\text{H}_3^+ + \text{CH}_2^+ + \text{HCO}$	0.00272	± 0.00028
$\text{H}_3^+ + \text{C}_2\text{HO}^+ + 2\text{H}/\text{H}_2$	0.00104	± 0.00011

1-Propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$)



Supplementary Figure 9. Truncated coincidence time-of-flight spectrum of 1-propanol. The CTOF spectrum from dissociative ionization of 1-propanol in a linearly polarized laser focus of $2.0 \times 10^{14} \text{ W cm}^{-2}$. The magnified view of H^+ , H_2^+ , and H_3^+ formation channels is given in the inset. The logarithmic color scale indicates the number of events recorded.

Detection efficiency: $\varepsilon = 0.254 \pm 0.025$

Branching ratios:

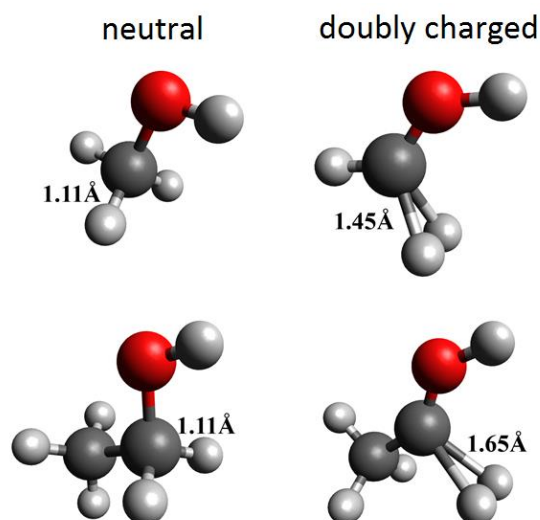
Sum of H_3^+ channels	$0.00250^{+0.00250}_{-0.00027}$	
$\text{H}_3^+ + [\text{C}_3\text{H}_3^+ + \text{H}_2\text{O} \text{ or } \text{C}_3\text{H}_2^+ + \text{H}_3\text{O}]$	0.0008910	± 0.0000973
$\text{H}_3^+ + \text{C}_3\text{H}_3\text{O}^+ + 2\text{H}/\text{H}_2$	0.0006491	± 0.0000673
$\text{H}_3^+ + \text{C}_3\text{HO}^+ + 4\text{H}$	0.0004833	± 0.0000507
$\text{H}_3^+ + \text{C}_2\text{H}_3^+ + \text{CH}_2\text{O}$	0.0001378	± 0.0000647
$\text{H}_3^+ + \text{C}_3\text{H}_2\text{O}^+ + 3\text{H}$	0.0001250	± 0.0000149
$\text{H}_3^+ + \text{CHO}^+ + \text{C}_2\text{H}_4$	0.0001169	± 0.0000540
$\text{H}_3^+ + \text{C}_3\text{H}_4\text{O}^+ + \text{H}$	0.0000689	± 0.0000099
$\text{H}_3^+ + \text{C}_3\text{H}_5\text{O}^+$	0.0000295	± 0.0000052

No single dications were identified in the 1-propanol TOF spectrum (see Supplementary Fig. 3). As a result, the detection efficiency plays no role in evaluating the branching ratios of this dication. Note that the detection efficiency evaluated from the propanol run is much lower than for the other runs, suggesting possible losses of $\text{H}_3^+ + \text{ion}$ (+ neutral) events or the production of H_3^+ from the monocation of propanol. We have estimated the losses in the main $\text{H}_3^+ + \text{ion}$ channel, in order to place an

upper limit on the total H_3^+ production branching ratio, which may be somewhat higher than the 0.0025 reported above. At most, the losses are about 50%, therefore the upper limit of the “Sum of H_3^+ channels” is 0.005, which is still a factor of 5.5 smaller than in ethanol. Therefore, we report this branching ratio as 0.0025 with a positive error estimated to be 0.0025 and a negative error of 0.00027. We should note that the positive error is dominated by the losses and is a maximum error, while the negative error is at the one sigma level and includes the same error sources as for the methanol and ethanol, listed before. Another consequence of this error analysis is that it supports the assertion that some of the H_3^+ is formed from the 1-propanol monocation and not just the dication as is the case for methanol and ethanol.

Supplementary Note 3 – *Ab initio* electronic structure calculations

A comparison of the neutral and doubly-charged minima of methanol and ethanol is shown in Supplementary Fig.10 and was carried out at the CCSD/aug-cc-PVDZ level of theory. It is worth noting that diffuse basis functions were required to obtain the doubly-charged minimum, especially for ethanol, where the C–H bonds were elongated. Similar stable structures were observed for methanol with larger (aug-cc-PVTZ and aug-cc-PVQZ) basis sets. However, a stable doubly-charged structure was not found for ethanol when the larger aug-cc-PVTZ and aug-cc-PVQZ bases were employed. During optimizations with these sets the two elongated C–H bonds were broken forming a separate H₂ molecule. Our past dynamic simulations of methanol and these optimizations both suggest that the potential energy surface is quite flat in this region, and therefore the presence or absence of a true minimum is of little consequence. Whether or not a true minimum exists, these structures represent an important point along the path to H₂ formation, and we continue to investigate it as such. Despite significant effort, no stable doubly-charged minimum structures were identified for 1- or 2-propanol. Alpha cleavage occurred during optimization of these systems. Note also that the optimized doubly-charged structures presented are not the global minima on the dication potential energy surfaces. Lower energy structures are observed with the H atom of the alcohol group rotated 180 degrees into an eclipsed conformation. However, in our prior molecular dynamics study, such rotation was not observed. Thus, we focus here on the local minima closest to the staggered global neutral minimum energy structure.



Supplementary Figure 10. Neutral and doubly-charged structure minima of methanol and ethanol along with the bond lengths of the C–H bonds that are involved in the roaming H₂ formation mechanism.

All (x, y, z) positions are in Angstroms.

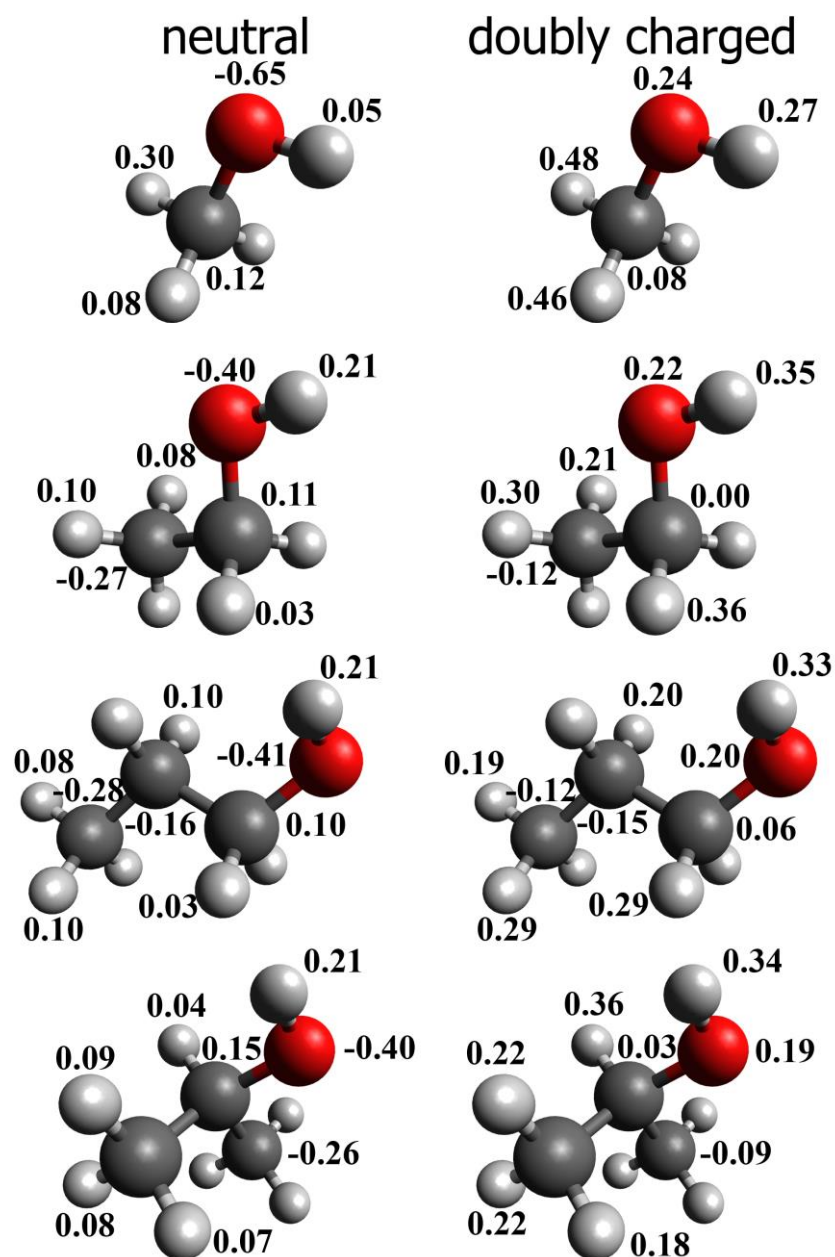
	x	y	z
Methanol CCSD/aug-cc-pVDZ structure:			
C	0.0000000195	-0.0131768233	-0.7343922430
H	-0.0000071776	1.0230451559	-1.1041231549
H	0.9012636481	-0.5256519967	-1.1187662006
H	-0.9012569859	-0.5256640351	-1.1187656406
O	0.0000000164	0.0642150004	0.6960184904
H	0.0000000220	-0.8340172099	1.0447990281

Methanol²⁺ CCSD/aug-cc-pVDZ structure:			
C	0.1189100179	0.0000430246	0.5905496163
H	1.0313154368	0.0001752224	1.2430077346
H	-1.0531236166	0.4383414673	1.3285827728
H	-1.0530053232	-0.4386474885	1.3285737727
O	0.0290167368	-0.0000620036	-0.6135424060
H	-0.8027571896	0.0006023057	-1.1983973794

Ethanol CCSD/aug-cc-pVDZ structure:			
C	0.5823320567	0.0000006934	0.0068561207
H	1.2316304512	0.8963327894	0.0401338985
H	1.2316318110	-0.8963302897	0.0401359596
O	-0.3266327451	0.0000013928	1.1199442120
H	0.1891694455	-0.0000207052	1.9340413694
C	-0.2532427341	-0.0000009016	-1.2680477372
H	0.4036223760	0.0000294370	-2.1551061844
H	-0.8964028113	-0.8950767849	-1.3038375078
H	-0.8964450418	0.8950459252	-1.3038078383

Ethanol²⁺ CCSD/aug-cc-pVDZ structure:			
C	0.2215308728	0.0004025632	0.0444691126
H	1.8243587117	0.4100894434	0.1128925228
H	1.8225276032	-0.4109498723	0.1112697220
O	-0.2382919152	-0.0000507140	1.1546073811
H	0.2056842234	-0.0008655943	2.0593889450
C	-0.1658509121	0.0000191134	-1.3506316157
H	0.2684836791	-0.9097264325	-1.8358787519
H	-1.2797579380	0.0050777582	-1.3693431502
H	0.2776945931	0.9021548395	-1.8411003929

The neutral structure minima of the four alcohols were also obtained at the CCSD/cc-pVQZ level of theory. At the neutral structure minima, the density matrix and Mulliken population analysis were evaluated for neutral and doubly-charged electronic configurations at the EOM-CCSD/cc-pVQZ level of theory. This allows us to probe the change in electron density under the assumption of an instantaneous (much faster than nuclear rearrangement) double ionization. Atomic charges for both electronic configurations are depicted in Supplementary Fig. 11.



Supplementary Figure 11. Mulliken atomic charges of methanol, ethanol, 1-propanol, and 2-propanol (top to bottom) for the neutral and doubly-charged electronic configurations. Atomic charges on atoms that are equivalent by symmetry are not shown.

All (x, y, z) positions are in Angstroms.

	x	y	z
Methanol CCSD/cc-pVQZ structure:			
C	0.0000000694	-0.0132012215	-0.7243533803
H	-0.0000229410	1.0070988969	-1.0967123079
H	0.8882245538	-0.5188207406	-1.1076907792
H	-0.8882033680	-0.5188591048	-1.1076888181
O	0.0000000565	0.0637854542	0.6871491326
H	0.0000000316	-0.8245980541	1.0363955536

Ethanol CCSD/cc-pVQZ structure:			
C	0.5741964862	0.0000010542	0.0097229849
H	1.2176776373	0.8835033672	0.0396304336
H	1.2176781238	-0.8835006756	0.0396329899
O	-0.3230829773	0.0000021071	1.1082310436
H	0.1851242443	-0.0000310863	1.9168350897
C	-0.2487682980	-0.0000013115	-1.2572665551
H	0.3990380445	0.0000459135	-2.1327591430
H	-0.8844826432	-0.8825184153	-1.2942669471
H	-0.8845484542	0.8824705151	-1.2942206836

1-Propanol CCSD/cc-pVQZ structure:			
C	0.4930178502	-0.0249404907	0.5382662111
H	1.1626047753	0.8315684531	0.4691154338
H	1.1080542798	-0.9263216560	0.4475173667
O	-0.0966631449	0.0532492160	1.8227097378
H	-0.6722992419	-0.7018955823	1.9329465254
C	-0.5248461452	0.0212641769	-0.5870540632
H	-1.2040986537	-0.8299502239	-0.4893294041
H	-1.1290408202	0.9220009357	-0.4739439700
C	0.1425395256	-0.0052700172	-1.9562967112
H	0.7423506609	-0.9067848773	-2.0842995761
H	-0.5948891807	0.0197494086	-2.7564111722
H	0.8024100820	0.8529971896	-2.0847756021

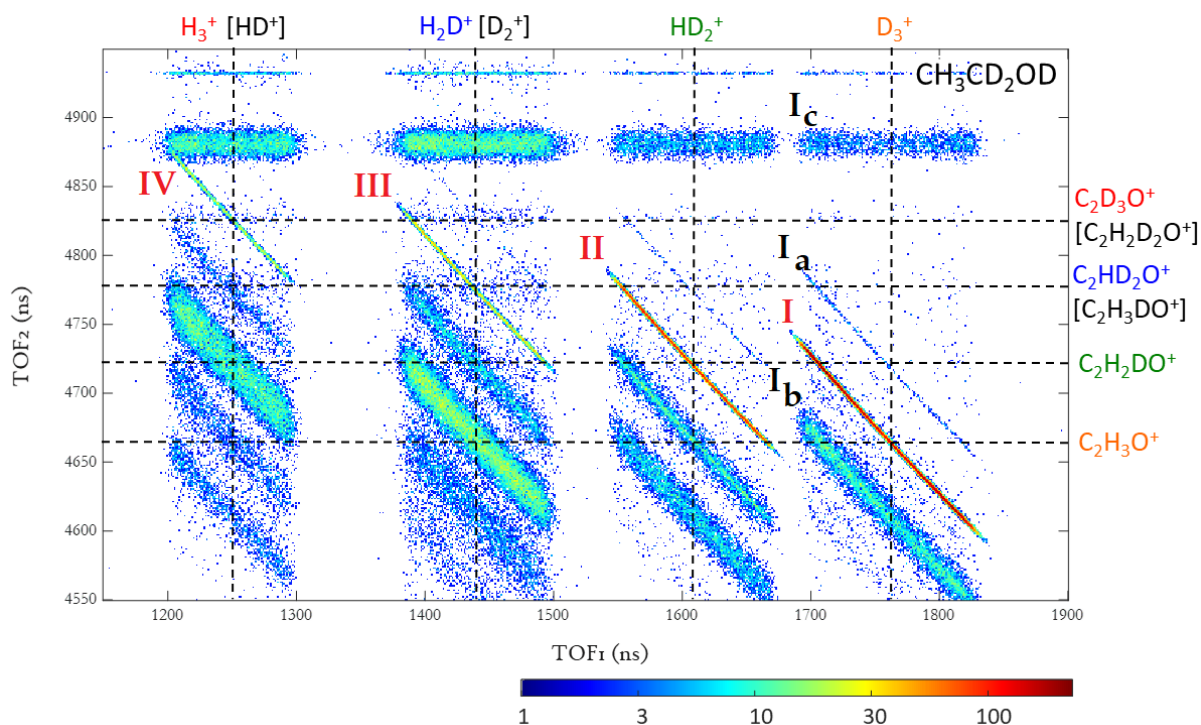
2-Propanol CCSD/cc-pVQZ structure:			
C	-0.0159115345	0.3695240977	0.0066974781
H	0.0097040168	1.4647090165	0.0083600582
O	1.3066595780	-0.1324317989	-0.1328388204
H	1.8149854532	0.1399616563	0.6299247250
C	-0.6488330620	-0.1128198868	1.3007613359
H	-1.6623032797	0.2744247409	1.4038547201
H	-0.6873525459	-1.2016692465	1.3137227831
H	-0.0735326642	0.2210004244	2.1653994638
C	-0.7812832287	-0.1001014046	-1.2121787195
H	-1.8010911859	0.2819061196	-1.1947719236
H	-0.2938692287	0.2446418896	-2.1216589733
H	-0.8162028895	-1.1889754161	-1.2316258925

When comparing the neutral and the doubly-charged configurations, one can clearly see that the largest increase in the positive charge on the H atoms within a molecule is associated with the ones that are on the α -C. This change is larger for the two H atoms that are *gauche* relative to the H atom of the alcohol group compared to the *anti*-H in the case of methanol. Moreover, the H atoms of methanol exhibited larger increase in positive charge than those of ethanol. This charge thus correlates with the experimentally observed H_3^+ yields.

All CCSD geometry optimizations were carried out using Molpro 2012.1⁵⁻⁷ software package while the EOM-CCSD part was calculated using GAMESS^{8,9}.

Supplementary Note 4 – New H_3^+ formation pathways

Here we discuss the features and important information pertaining to the proper identification of H_3^+ formation pathways from CTOF spectra shown in Fig. 3 of the main text. As an example, we use the CTOF spectrum from the dissociative ionization of CH_3CD_2OD (Fig. 3(a) of main text), which is also shown as Supplementary Fig.12.



Supplementary Figure 12. H_3^+ formation from ethanol. Truncated coincidence time-of-flight map focused only on H_3^+ production in two-body channels from dissociative ionization of CH_3CD_2OD in a linearly polarized laser pulse centered about 790 nm, 23-fs long with a peak intensity of $3.0 \times 10^{14} \text{ W cm}^{-2}$. The logarithmic color scale depicts the number of ion pairs recorded.

Among several coincidence channels visible on the CTOF map shown in Supplementary Fig. 12 (contour regions at the intersections of vertical and horizontal dashed lines with an approximate slope of -1), our attention primarily focused on four channels, which are sharp thin contour regions labeled as I, II, III, and IV. These channels correspond to true two-body breakup ion pairs related to H_3^+ formation from the ethanol dication, which conserve momentum during photodissociation. For instance, the channel labeled by I represents $\text{CH}_3\text{CD}_2\text{OD}_2^{2+} \rightarrow \text{C}_2\text{H}_3\text{O}^+ + \text{D}_3^+$ and channel II represents $\text{CH}_3\text{CD}_2\text{OD}_2^+ \rightarrow \text{C}_2\text{H}_2\text{DO}^+ + \text{HD}_2^+$. Due to mass-to-charge degeneracy in H_2D^+ ($m/z = 4$) and D_2^+ ($m/z = 4$) ions, the two-body breakup channels corresponding to the formation of these two ions, $\text{CH}_3\text{CD}_2\text{OD}_2^+ \rightarrow \text{C}_2\text{HD}_2\text{O}^+ + \text{H}_2\text{D}^+$ and $\text{CH}_3\text{CD}_2\text{OD}_2^+ \rightarrow \text{C}_2\text{H}_3\text{DO}^+ + \text{D}_2^+$ respectively, become indistinguishable in the CTOF map and are labeled as III. Similarly, the channel labeled by IV represents two degenerate two-body breakup channels corresponding to the formation of H_3^+ and HD^+ .

Apart from the above four two-body breakup ion-pair channels, there are many other channels visible on the CTOF map. The channel represented by the label I_a is due to isotopic impurity in the sample. This is typically due to the natural occurrence of ^{13}C at the 2.2% level in the sample (since the probability of a given C atom being ^{13}C is 1.1% due to natural abundance). Wide and dispersed contour regions on the CTOF map correspond to breakup channels involving more than two breakup partners, typically involving an ion pair and a third fragment that is predominantly neutral (uncharged). For instance, the channel labeled by I_b corresponds to the three-body breakup $\text{CH}_3\text{CD}_2\text{OD}_2^{2+} \rightarrow \text{C}_2\text{H}_2\text{O}^+ + \text{D}_3^+ + \text{H}$. The spread of the channel width is defined by the momentum absorbed by the third fragment during the photodissociation process. Horizontal contour regions, e.g. channel I_c , represent false (random) coincidences, where the paired ions arise from two separate parent dications in the focal region produced by the same laser pulse. These false events contain no useful information in quantitative analysis of CTOF spectra and can be removed (see Supplementary Note 1 (iii) for more information).

Supplementary Note 5 – *Ab initio* molecular dynamics simulations

Assessment of the validity of QCISD *ab initio* molecular dynamics for H_2 and H_3^+ formation is carried out on methanol and compared to our previous CASSCF results¹ as summarized in Supplementary Table 2. We notice that QCISD was incapable of predicting the formation of H_2^+ due to the open shell nature of that fragment. On the other hand, H_2 and H_3^+ formation yields were higher than CASSCF. This bias towards closed shell fragments provides a higher probability to observe the H_3^+ formation in ethanol which wasn't observed using CASSCF.

Supplementary Table 2. Percentage of hydrogen species (summed over all channels) ejected from doubly-charged methanol that are observed using CASSCF and QCISD *ab initio* molecular dynamics simulations.

	CASSCF % Yield	QCISD % Yield
H^+ formation	48.3	43.9
H_2^+ formation	23.4	0
H_2 formation	18.8	40.3
H_3^+ formation	4.0	5.4

Supplementary References

1. Ekanayake, N. *et al.* Mechanisms and time-resolved dynamics for trihydrogen cation (H_3^+) formation from organic molecules in strong laser fields. *Sci. Rep.* **7**, 4703 (2017).
2. Linusson, P. *et al.* Double photoionization of alcohol molecules. *Phys. Rev. A* **80**, 1–6 (2009).
3. Ben-Itzhak, I., Carnes, K. D., Johnson, D. T., Norris, P. J., & Weaver, O. L. Fragmentation of CH_4 caused by fast-proton impact. *Phys. Rev. A* **47**, 3748 (1993).
4. Ben-Itzhak, I., Carnes, K. D., Johnson, D. T., Norris, P. J. & Weaver, O. L. Velocity dependence of ionization and fragmentation of methane caused by fast-proton impact. *Phys. Rev. A* **49**, 881 (1994).
5. Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M., Molpro: a general-purpose quantum chemistry program package. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* 2012, **2**, 242-253.
6. *MOLPRO, version 2012.1, a package of ab initio programs* H.-J. Werner, P. J. K., G. Knizia, F. R. Manby, M. Schütz, P. Celani, W. Györffy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang. see <http://www.molpro.net>.

7. Hampel, C.; Peterson, K. A.; Werner, H.-J., A comparison of the efficiency and accuracy of the quadratic configuration interaction (QCISD), coupled cluster (CCSD), and Brueckner coupled cluster (BCCD) methods. *Chem. Phys. Lett.* **190**, 1-12 (1992).
8. Piecuch, P.; Kucharski, S. A.; Kowalski, K.; Musiał, M., Efficient computer implementation of the renormalized coupled-cluster methods: The R-CCSD[T], R-CCSD(T), CR-CCSD[T], and CR-CCSD(T) approaches. *Comp. Phys. Commun.* **149**, 71-96 (2002).
9. Włoch, M.; Gour, J. R.; Kowalski, K.; Piecuch, P., Extension of renormalized coupled-cluster methods including triple excitations to excited electronic states of open-shell molecules. *J. Chem. Phys.* **122**, 214107 (2005).