

Probing the structure and dynamics of complex hydrocarbons with ionizing
radiation from free-electron lasers

by

Kurtis Borne

B.Sc., University of Nebraska-Omaha, 2016

AN ABSTRACT OF A DISSERTATION

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requirements for the degree

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Department of Physics
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Abstract

Directly imaging the ultrafast changes in molecules during photochemical reactions has been a long-standing goal for chemists and physicists. Over the past three decades, ultrafast and intense light sources, including free-electron lasers (FELs), have been developed. These tools have enabled measurements that can probe the structure and dynamics of photoexcited molecules with femtosecond time-resolution. As these light sources improved, photo and electron spectroscopies have likewise developed, enabling high-dimensional measurements that provide a wealth of information on light-matter interaction.

In this thesis, FELs operating from the extreme ultraviolet (XUV) to the X-ray regime are used to study the electronic and structural properties of complex isolated molecules. Specifically, ultrafast electronic relaxation processes of the quadricyclane molecule are explored. This highly strained molecule and its isomer, norbornadiene, are photoswitches with promising candidacy for solar energy storage. Here we apply time-resolved photoelectron spectroscopy at a highly coherent XUV-FEL. The experimental results are combined with non-adiabatic molecular dynamic simulations. With the high photon energy XUV-FEL source, we are able to monitor the molecule from any electronic state involved in the photochemical reaction, and we observe two competing relaxation pathways. One pathway is distinguished by a coupling to several valence electronic states that return the system to the ground state within ~ 100 femtoseconds. The other pathway involves slower motion along the long-lived Rydberg states. Both pathways facilitate isomerization with a predicted branching ratio of norbornadiene/quadricyclane at approximately 3:2 in the electronic ground state.

Secondly, Coulomb explosion imaging (CEI) is discussed. This experimental technique applies coincidence momentum imaging of molecules that rapidly dissociate after being

photoionized to a highly-charged state. This technique has generated a lot of excitement as it is a promising candidate for probing gas-phase molecular structures, with previous results showing a beautiful molecular frame picture¹. In this thesis, we apply this technique to isomers with different cyclic geometries, demonstrating that CEI can differentiate gas phase hydrocarbon isomers that contain no preferential X-ray absorption sites, nor unambiguous ways to define a molecular frame due to the absence of *marker* ion momenta. This work contributes to the understanding of ultrafast molecular dynamics that underlies several light-induced biological processes, and potential applications in the optical control of quantum molecular systems.

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Approved by:

Major Professor
Daniel Rolles

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Good luck and godspeed...

Kurtis

Chapter 1

Introduction

It seems that so many important natural phenomena occur on timescales too short for human perception. From the galloping of a horse² to vitamin photosynthesis³, the intricacies of the motion in these biological systems are too fast to be viewed by our naked eye. Only in recent history has human ingenuity and engineering developed methods to study these systems at their natural timescales. The best methods are those that directly capture an unambiguous image of the changing system.

Even the way a horse gallops had been elusive for years. Before the 19th century, riders and artists held a perception that the animal leapt with all four limbs fully extended in a swift, graceful motion. For centuries romantic paintings depicted horses with an exaggerated ‘flying gallop’.

Noted American attorney and former California governor, Amasa Leland Stanford, who raised several horses on his California farm in the 1870s, had his doubts. In 1881, he wrote; “I have for a long time entertained the opinion that the accepted theory of the relative positions of the feet of horses in rapid motion was erroneous. I also believed that the camera could be utilized to demonstrate that fact, and by instantaneous pictures show the actual position of the limbs at each instant of the stride.^{2”} So, he hired photographer Eadweard Muybridge to setup a series of closely separated cameras that would be triggered by a cart the horse



Figure 1.1: Artist depiction of a horses gallop before the work of Muybridge and Stanford. Théodore Géricault, *Derby at Epsom*, 1821, oil on canvas, 92 x 116 cm (Musée du Louvre).⁴

pulled as it galloped. The cameras would thus capture the motions within the horses stride. What they observed from the series of photographs greatly contradicted the picture people had. Rather than the graceful leap, the horses legs moved in a complex interleaving motion under its body.

The methodology with which Stanford approached this problem aligns with the what physicists and chemist do to study the ultrafast changes in atomic and molecular systems. Instead of flash cameras, we want to use ultrashort light pulses to project the system into a state that provides an instantaneous, unambiguous observable that encodes the actual position of atoms within the ‘stride’ of an excited molecule.

The development of such methodologies is challenging because molecular motion occurs on incomprehensibly fast femtosecond timescales ($1/1,000,000,000,000$ of a second). Analogies drawn from everyday human activities fall short when compared to femtosecond molecular dynamics. Suffice it to say, that the speed at which a carbon ring opens in vitamin-D3



Figure 1.2: “*The Horse in Motion*”: Series of images capturing the true mechanism of a horses gallop. From “*The Horse in Motion*.” (Sallie Gardner, Owned by Leland Stanford; Running at a 1:40 Gait Over the Palo Alto Track, 19th June 1878), 1878. Library of Congress Prints and Photographs Division⁵

photosynthesis in relation to the timescales of human perception, is comparable to the speed of a horse stride in relation to the timescale of all human history.

The field of femtochemistry was first pioneered by Egyptian-American scientist Ahmed H. Zewail at the California institute of technology in 1988⁶. This field set out to observe chemical reactions that occur at these fast timescales. Employing intense ultrafast lasers, Zewail performed measurements that could observe chemical transition states on femtosecond timescales, such as the making or breaking of chemical bonds. For his revolutionary work he was awarded the 1999 Nobel Prize in chemistry⁷.

Near the same time in 1987, French physicist Anne L’Huillier, developed theories for high harmonic generation of light in rare gases^{8,9}. This development would later be independently used by Hungarian physicist Ferenc Krausz and French physicist Pierre Agostini to generate attosecond light pulses ($1/1,000,000,000,000,000,000$ of a second)^{10,11}. Just as Zewail’s work enabled the direct observation of nuclear motion in molecules, the work of L’Huillier, Krausz, and Agostini enabled the direct observation of electron motion. For these accomplishments, the three won the 2024 Nobel Prize in physics¹².

Several techniques have been applied to study photochemistry using time-resolved spec-

troscopies. These techniques employ an excitation light pulse that ‘pumps’ the molecular sample to an excited state on which its wavepacket evolves. This is followed by a ‘probe’ pulse. This probe can project the molecular wavepacket into another state that provides an observable that encodes information of the ultrafast evolution, as is the case for transient absorption or photoelectron spectroscopies^{13,14,15,16,17,18,19,20}. Other methods employ direct observation of how this probe changes when it interacts with a sample. This is the case of coherent x-ray scattering or ultrafast electron diffraction^{21,22,23,24}. The theoretical framework of time-resolved techniques, particularly for photoelectron spectroscopy, is discussed in chapter 2.

Several of these techniques have benefited from the use of X-ray Free Electron Lasers (FELs)^{25,26}. These large facilities provide intense, ultrashort X-ray pulses with lasing mechanisms akin to intense table-top lasers. All the work in this thesis was conducted at FELs for probe pulses in the extreme ultraviolet (10 to 100 eV) or soft X-ray (100 to 5000 eV) ranges. These high-energy photons are able to remove electrons from molecules through different ionizing processes.

All the work in this thesis involves detection of the photoparticles formed from photon-matter interaction. Several of these experiments include measuring the three-dimensional momentum of several photoparticles and seeing how they correlate with each other. In some experiments, it was necessary to measure properties of the X-ray pulse at the same time as the photoparticle detection for correlation analysis that improves temporal or energy resolution. These high dimensional measurements have necessitated the development of sophisticated analysis. Chapter 3 includes a discussion of free-electron laser principles, the spectrometer techniques to study the photoparticles they generate, and the sophisticated analysis necessary to fully elucidate the probing process.

That chapter includes two manuscripts that are in review at the time of writing this thesis. Section 3.4 includes a manuscript on the design and performance of the recently modified magnetic bottle electron spectrometer at the Linac Coherent Light Source (LCLS) FEL at

Stanford’s SLAC institute. Section 3.5 includes a manuscript on a detector correlation technique to improve the pump-probe resolution in experiments where the synchronization between the two pulses is unstable and the acquisition of the main detector is sub-optimal.

The comprehensive goal of the other experiments is to study the structure and photoexcited dynamics of hydrocarbon isomers with the chemical formula C_7H_8 . These molecules have the same formula but different molecular geometries. Understanding the photochemistry of these molecules is important because they have potential applications in energy storage, as described in chapter 4. In that chapter, studying the interconversion of these isomers using time-resolved photoelectron spectroscopy with XUV pulses from a seeded FEL to probe the photoexcited dynamics of one of these isomers, quadricyclane. This measurement was able to monitor the molecules photoexcited evolution, from the excited state manifold all the way to the ground state, and monitor any subsequent interconversion to its isomeric counterpart, norbornadiene. This chapter includes a published paper (section 4.2.1) describing these results which contains theoretical support¹⁹.

The other isomers of C_7H_8 provide a good test-case for imaging the unique molecular geometries that may occur during a photoreaction, as in the case for chapter 5. These measurements employ X-ray induced Coulomb explosion imaging (CEI) to distinguish the different isomers, and map the momenta of correlated photoions back to the molecular geometries^{1,27,28,29}. This chapter demonstrates the efficacy of employing CEI for biologically relevant molecules that are pure hydrocarbons.

Lastly, chapter 6 contains a summary and outlook related to studies presented in this thesis. That chapter contains a brief description of several spectroscopic tools being developed at the LCLS-II.

Chapter 2

Probing the dynamics of molecules with photoelectron spectroscopy

The basics of molecular structure and photoexcited dynamics of simple molecules will be presented in this chapter. First we introduce the standard quantum chemistry formalisms for molecular wavefunctions, then we discuss the basics of molecular photoexcitation and ionization schemes that are relevant to the work in this thesis. Lastly we discuss the theory behind time-resolved photoelectron spectroscopy and its associated experimental techniques that are relevant for the subsequent chapters. Note, that unless otherwise specified, this section uses atomic units $e = m_e = 4\pi\epsilon_0 = 1$, Where e and m_e are the electric charge and mass of the electron, respectively, and ϵ_0 is the vacuum permittivity.

2.1 Molecular electronic structure

The quantum mechanical wavepacket of a photoexcited molecule is complex due to the interactions between all negatively charged electrons and positively charged atomic nuclei. The Hamiltonian of a molecule can be written as

$$\begin{aligned}
H &= \left(-\sum_{i=1} \frac{\nabla_{\mathbf{r}_i}^2}{2m_i} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{2} \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right) + \left(-\sum_{I=1} \frac{\nabla_{\mathbf{R}_I}^2}{2M_I} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \right) \\
&= H_e + H_n
\end{aligned} \tag{2.1}$$

The position of the i^{th} electron is denoted with $(\mathbf{r}_i)$, while the position of the I^{th} nucleus is denoted with $(\mathbf{R}_I)$. The mass and charge of the i^{th} nuclei are denoted M_i and Z_i , respectively. Note that the summation in eq. 2.1 is split into two parts, with the right term depending only on the nuclear coordinates. This splits the Hamiltonian into an electronic, (H_e) , and a nuclear (H_{nuc}) part.

The initial molecular wavefunction can be found by solving the time-independent Schrödinger equation,

$$H\psi(r, R) = E\psi(r, R) \tag{2.2}$$

The total molecular state can be expressed approximately as a finite linear combination of known basis functions,

$$\psi(r, R) = \sum_k \Theta_k(\mathbf{R}) \phi_k(\mathbf{r}; \mathbf{R}). \tag{2.3}$$

Generally, these basis functions are the electronic states, and are eigenstates of the purely electronic Hamiltonian,

$$H_e \phi_k(\mathbf{r}) = \epsilon_k \phi_k(\mathbf{k}). \tag{2.4}$$

These basis functions can be found by solving eq. 2.4. Often, a self consistent Hartree-Fock method is used by formulating $\phi_k(\mathbf{k})$ as a linear combination of *Slater determinants*

which builds a solution to eq. 2.4. These Slater determinants are anti-symmetric functions formed by products of single electron orbital wavefunctions that include both spatial and spin components. The respective electronic wavefunction are functions of the electronic coordinates, $\mathbf{r}$, but they will be parameterized by the nuclear coordinates, $\mathbf{R}$ (denoted by the semi-colon in eq. 2.3). This is due to the nuclear coordinates being held fixed in the electronic Hamiltonian (eq. 2.4). In the case that $\mathbf{R}$ changes, then $\phi_k(\mathbf{r})$ and ϵ_k will need to be solved for again. The expansion coefficients $\Theta_k(\mathbf{R})$, are the nuclear wavefunctions, and are functions of the nuclear coordinates only. Regardless of how $\phi_k(\mathbf{r})$ and ϵ_k are determined, $\Theta_k(\mathbf{R})$ have yet to be solved.

To make solving eq. 2.2 feasible, the Born-Oppenheimer approximation is applied. In this adiabatic approximation, the electrons will respond quickly to small changes in the nuclei positions. This assumption is valid because of the enormity of the nuclei mass compared to the electron, and it enables separability in the electronic and nuclear wavefunctions.

Substituting eq. 2.3 into eq. 2.1 and projecting onto an orthonormal state $\psi'(\mathbf{r}, \mathbf{R})$, reveals cross-terms which are non-adiabatic, signifying coupling among different electronic states. These terms are ignored through the Born-Oppenheimer approximation, and it can be shown that the corresponding separability in electronic and nuclear coordinates reveals an eigensystem for the nuclear wavefunction^{30,31}

$$\left(- \sum_i \frac{\nabla_{R_i}^2}{2M_I} + U_{nuc}(\mathbf{R}) \right) \Theta_k = E \Theta_k, \quad (2.5)$$

where the nuclear potential energy surface is defined as

$$U_{nuc}(\mathbf{R}) = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \epsilon_k. \quad (2.6)$$

With the adiabatic approximations discussed, eq. 2.5 is the Schrödinger equation for the nuclear wavefunction that can be solved numerically.

It is important to note that these potential energy surfaces in eq. 2.6 dictate the nuclear

motion when excited out of their equilibrium configurations. Building these potential energy surfaces along the adiabatic coordinates defines the vibrational states. Solving for this potential for different electronic configurations k , even those for ionic states, will build separate excited state potential energy surfaces that may have significantly different gradients compared to the molecular ground state.

In regions where these potential energy surfaces become degenerate, the molecular wavepacket can move between these surfaces, effectively relaxing the molecular system without absorbing or emitting radiation. These regions on the potential energy surfaces are called conical intersections. It is in this region where the assumed adiabatic principles break down and the nuclei positions can rapidly change in response to the wavepacket moving from one region of the potential energy surfaces to another^{32,33}.

2.2 Photoexcitation of molecules

If the molecule absorbs a photon with adequate energy it can be excited to a higher lying electronic state and the wavepacket will move to a higher lying potential energy surface. This optical transition is very fast in comparison to any nuclear motion. Thus the transition is *vertical*, and the wavepacket is approximated to be excited from one point on the initial potential energy surface to the same nuclear configuration on the excited-state surface. This approximation is known as the Franck-Condon principle.

The strength of the photoabsorption transition from the ground state ψ to the excited state ψ' is dictated only by the permanent electric dipole moment between the two states. In this transition the wavepacket not only moves to a higher lying potential energy surface $k \rightarrow k'$ (associated with dipole moment $\boldsymbol{\mu}_{ele}$), it may also move to a different nuclear vibration state $\nu \rightarrow \nu'$ (associated with dipole moment $\boldsymbol{\mu}_\nu$). Adhering to the adiabatic approximations, this can be derived as

$$\begin{aligned}
R_{\psi' \rightarrow \psi} &= \int \phi_{k'}^*(\mathbf{r}; \mathbf{R}) \Theta_{\nu'}^*(\mathbf{R}) (\boldsymbol{\mu}_{ele} + \boldsymbol{\mu}_{\nu}) \phi_k(\mathbf{r}; \mathbf{R}) \Theta_{\nu}(\mathbf{R}) d\mathbf{R} d\mathbf{r} \\
&= \int \Theta_{\nu'}^*(\mathbf{R}) \left[\int \phi_{k'}^*(\mathbf{r}; \mathbf{R}) \boldsymbol{\mu}_{ele} \phi_k(\mathbf{r}; \mathbf{R}) d\mathbf{r} \right] \Theta_{\nu}(\mathbf{R}) d\mathbf{R} \\
&+ \int \Theta_{\nu'}^*(\mathbf{R}) \boldsymbol{\mu}_{\nu} \left[\int \phi_{k'}^*(\mathbf{r}; \mathbf{R}) \phi_k(\mathbf{r}; \mathbf{R}) d\mathbf{r} \right] \Theta_{\nu}(\mathbf{R}) d\mathbf{R}
\end{aligned} \tag{2.7}$$

Because the states involved in the electronic transition are orthogonal for each value of $\mathbf{R}$, the integral in the second term goes to zero for $k \neq k'$. For transitions within the same electronic state $k = k'$, this term does not vanish. Assuming that the electronic dipole matrix element is a slow function of the nuclear coordinate, we replace the integration over electronic coordinates in parentheses by a constant evaluated at the equilibrium nuclear geometry,

$$R_{\phi \rightarrow \phi'} = \int \phi_k^*(\mathbf{r}; \mathbf{R}) \boldsymbol{\mu}_{elec} \phi_{k'}(\mathbf{r}; \mathbf{R}) d\mathbf{r}. \tag{2.8}$$

This electronic dipole transition can be removed from the integral and the nuclear dipole operation will not effect the electronic wavefuctions. So, the overall electric dipole moment is³⁴

$$\begin{aligned}
R_{\psi \rightarrow \psi'} &= R_{\phi \rightarrow \phi'} \int \Theta_{\nu'}^*(\mathbf{R}) \Theta_{\nu}(\mathbf{R}) d\mathbf{R} \\
&= R_{\phi \rightarrow \phi'} S(\nu', \nu)
\end{aligned} \tag{2.9}$$

The electric dipole transition moment is therefore strongest for vibrational states that have the greatest overlap along the internuclear coordinates in the ground state equilibrium. An example is shown in figure 2.1. The first two states (E_0 and E_1) have similar equilibrium internuclear distances, and hence effectively couple with a single vibrational state dictated

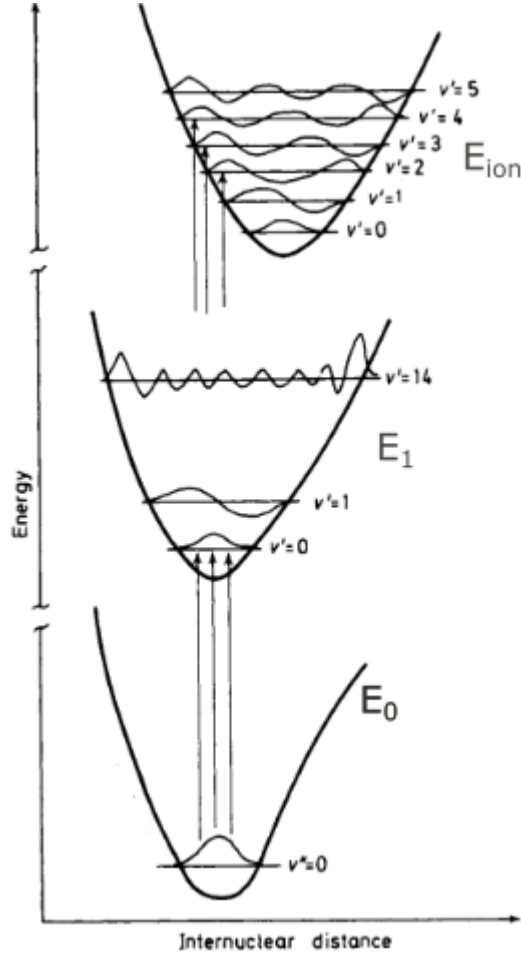


Figure 2.1: *Vibrational-wavefunctions are shown to illustrate the origin of the vibrational excitation in electronic transitions.*³⁵

by eq. 2.9.

Generally, values of the overlap integral $S(\nu', \nu)$ are found for a progression of vibrational states, and the transitions from the ground state occur with varying probabilities to all of them. These discretized progressions are observed in the electronic spectrum, as discussed in the next section.

Squaring the dipole transition moment provides the observable for the electron spectrum, particularly the relative intensity for a certain transition. For the adiabatic approximation, the square of the overlap integrals define the Franck-Condon factors, $|S(\nu', \nu)|^2$.

2.3 Photoionisation dynamics

If a molecule absorbs an adequately high energy photon it can transition to such a high lying state that the electron couples into the electronic continuum and the molecule is ionized. It is this electron that is detected, and its properties like kinetic energy, integrated flux, and angular distribution in the lab or molecular frame can be measured. For the work in this thesis, it is mainly the electron kinetic energy that is analyzed.

2.3.1 XUV ionization of valence electrons in molecules

The kinetic energy can be predicted in a very straightforward way with the application of *Koopman's theorem*. In this theorem, the first ionization potential of a molecule is equal to the negative of the energy of the highest occupied molecular orbital (HOMO). With the Hartree-Fock methods that treat the electrons as independent particles, the energy of the highest occupied orbital can be determined by solving for the eigenenergy in eq. 2.4.

Thus, the first ionization potential can be written as

$$I_p = -\epsilon_0 \quad (2.10)$$

This method can be used to solve the binding energy of any orbital, with the assumption that no other orbitals of the remaining electrons relax during the ionization process³⁶. This is a good approximation for outer valence electrons involved in bond formations. For inner valence and core electrons, this eq. 2.10 breaks down as there are significant electron correlations as the electron moves into the continuum³⁷.

The electron kinetic energy measured will be the difference in the incident photon energy and this ionization potential,

$$E_{kin} = \omega - I_p \quad (2.11)$$

For the photoelectron experiments conducted with the XUV ionizing source, it is the change of this binding energy after photoexcitation that is of interest, and with the energy-resolved electron spectroscopy technique employed, we use eq. 2.11 to determine the electron binding energy at different times during a photoreaction.

Again, putting Franck-Condon principles in the context of photoionization, the timescales of ionization are short compared to molecular vibrations. Furthermore, ionization can originate from transitions from the neutral to high lying vibronic states in the cation. If the equilibrium nuclear geometries between the neutral and cation are similar, the integral over the nuclear wavefunctions in eq. 2.9 is large, and the transition strength will be very strong.

If there is a substantial difference in the neutral and ionic equilibrium nuclear geometries, a vibrational progression in the electron spectra results from ionization of each neutral state to each ionic vibronic state. The schematic in fig. 2.1 illustrates this with the ionization from the neutral ground state E_0 to the ionic state E_{ion} where the minima of the curve is different between the two. In this example, coupling to the $\nu' = 0$ is negligible but $\nu = 2, 3$, and 4 are significant.

The photoelectron spectrum of the diatomic nitrogen N_2 demonstrates this mechanism clearly. Figure 2.2 shows the ground state potential energy curves and the three lowest ionic states above 15 eV in panel A. All three are accessible by photoionization with ~ 21 eV photon. The corresponding electron spectrum for each state are shown in panel B, each having distinguishing features. The highest and lowest ionic states, $X^2\Sigma_g^+$ and $B^2\Sigma_g^+$, respectively, are marked by single narrow peaks. This indicates that these ionic states have a similar equilibrium nuclear separation to that of the neutral ground state. The middle region associated with $A^2\Pi_u$ contains a series of peaks due to the slight offset in equilibrium separation between the ground and this ionic electronic states.

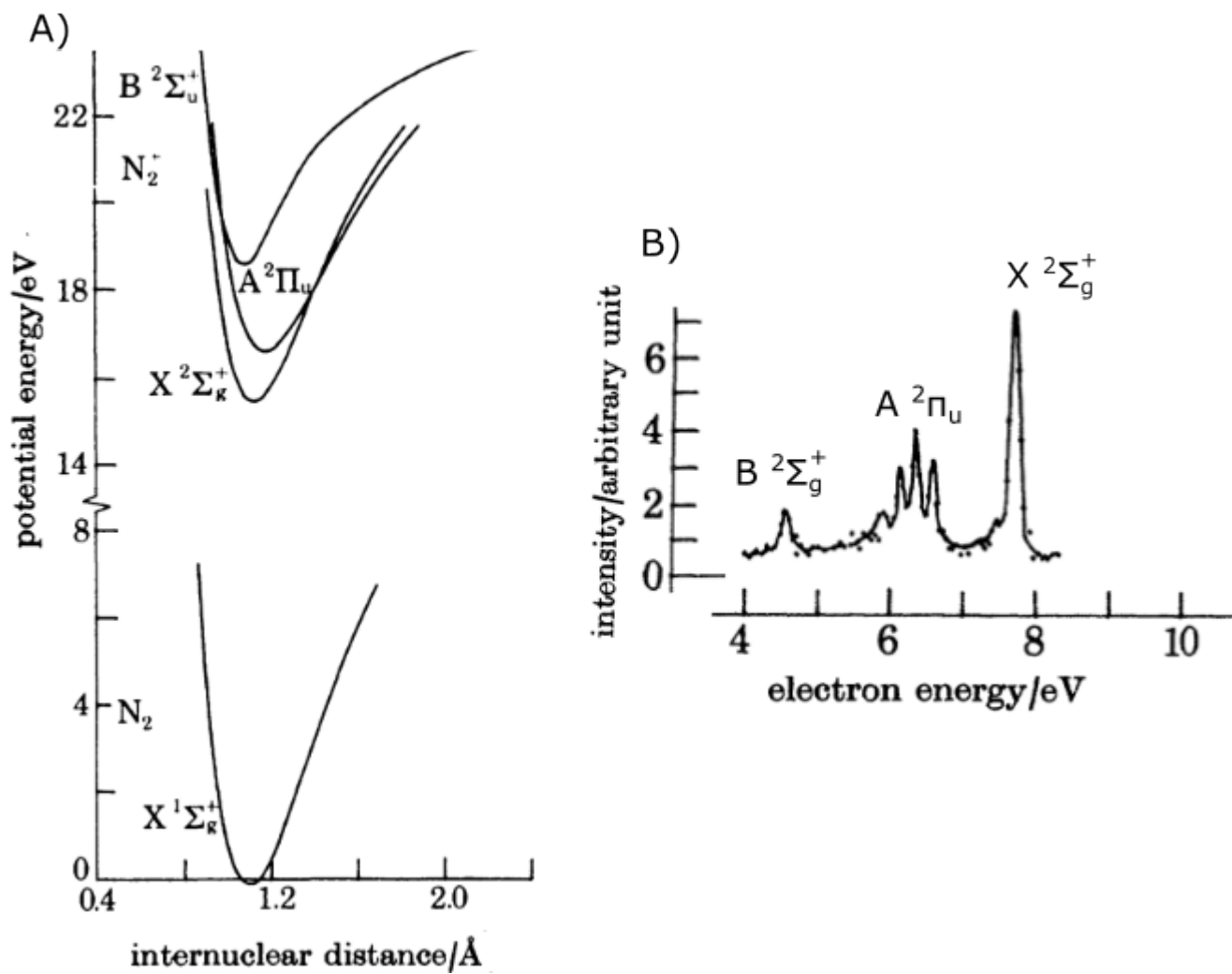


Figure 2.2: A) Potential energy curves for N_2 and N_2^+ . B) Photoelectron spectrum of N_2 ionized at 23 eV photon energy.³⁸

2.3.2 Photoionization with X-rays

When the photon energy is very high, ionization can occur in more deeply bound core orbitals for an atom in a molecule rather than the valence shells. Unlike the valence electrons, these inner shell electrons do not participate in bonding orbitals within the molecule and are energetically isolated from the other electrons. The electron density associated with these shells is well localized about a specific atomic site. Therefore, the ionization transition properties of these electrons behaves much like ionizing an atom with X-rays. Their binding energies are generally similar to the ionization energies for isolated atomic sites, except for a few eV chemical shifts.

When performing X-ray photoelectron spectroscopy, it is the properties of the absorption cross-section that enable site specificity in probing these electrons. It is easy to express this cross-section for a one-electron atom and generalize to multielectron atoms within a molecule. The partial cross sections for ionizing from a single sub-shells is defined with the electronic dipole moment, similar to the transition strength for molecular photoexcitation transitions in eq. 2.9,

$$\sigma_i(\omega) = \frac{1}{\omega} |\langle \phi_f^*(\mathbf{r}) | \mu_{elec} | \phi_i(\mathbf{r}) \rangle|^2 \quad (2.12)$$

The total photoionization cross section calculated by summing over all initial states, and for a single-electron atom with atomic number Z can be derived with the proportionality³⁹:

$$\sigma \approx Z^5 \omega^{-7/2}. \quad (2.13)$$

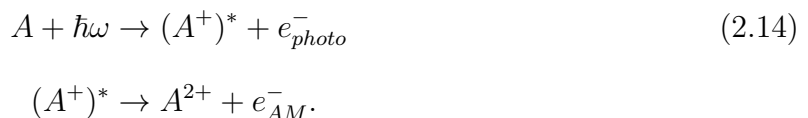
This shows that photoabsorption decreases with increasing photon energy. The Z^5 term demonstrates that heavier elements with a large Z value are much better X-ray absorbers than lighter ones with a lower Z value. The enormously different cross sections between atoms of even a single atomic number is the reason why x-ray photoelectron spectroscopy is *site-specific*, and can be used to monitor binding energy variations of a unique atom in

a molecule.

Auger-Meitner Decay

After the photoelectron (e_{photo}^-) is ejected from the atoms inner-shell (A) through X-ray photoionization, the molecule is left in an unstable excited state because of the remaining vacant core hole.

The excited state has two different ways in which it can relax. One way is for this molecule to eject a high energy photon during this transition. Alternatively, it can transfer the excess energy to another outer-shell electron, imparting enough energy that it is emitted from the molecule. No radiation is emitted in this scenario. Both scenarios involve an electron in a higher lying core orbital refilling the core-hole. In the latter case the second step is called Auger-Meitner (AM) electron emission e_{photo}^- ,



The kinetic energy of the AM electron is independent of photoexcitation energy. Rather it depends on the location of the initial core-hole and second outer hole in the dicationic molecule, with the difference in their energy levels being the kinetic energy of the AM electron. Two AM electrons can be produced in this process if the dication still has excess energy after the initial AM electron emission, a process called Auger-Meitner *cascade* ^{40,41,42}.

Because of the high ionization cross section and the AM-cascade effects that dominate the smaller atoms, X-ray sources can easily produce a highly ionized molecule with a single photon. With the development of XFEL sources that provide extremely high fluences, the X-ray intensity is so high that it can drive multiphoton absorption processes, with each absorption inducing more electron emissions ^{43,44,45}. These highly charged ionic states of

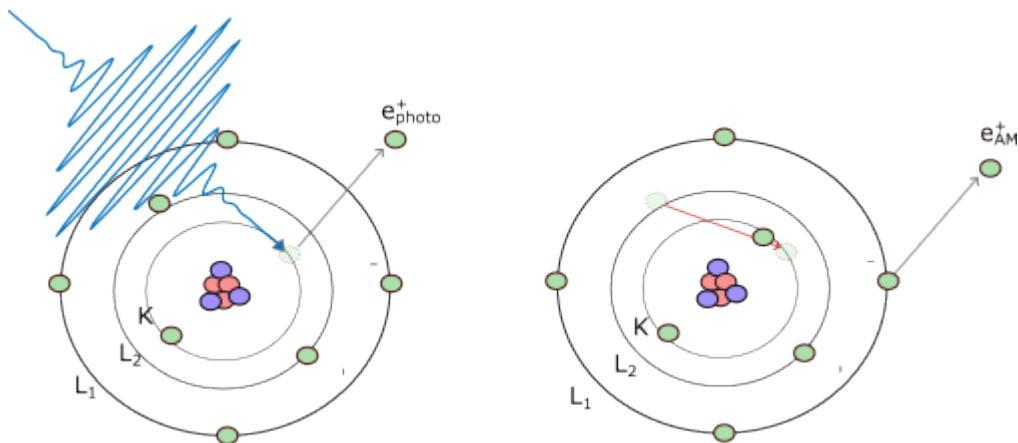


Figure 2.3: *The steps involved in Auger deexcitation.*

the molecules are unstable for the highly charged molecule and it will quickly fragment into several of its atomic constituents. Correlating these ionic fragments is the underlying principle of Coulomb explosion imaging, the topic of chapter 5.

2.4 Time-resolved photoelectron spectroscopy

The prototypical molecular systems that are discussed in this thesis are proposed to have applications to molecular switches and energy storage. The mechanism for these applications are induced by optical excitation, preferably at light wavelengths in the solar spectrum. To truly understand the underlying mechanisms in these molecular reactions, we want to monitor their electronic and nuclear evolution in the time domain. Time-resolved photoelectron spectroscopy (TRPES) is a good method for monitoring these molecular dynamics, as the photoelectron spectrum at each point in time may provide information on the electronic and nuclear structure of the excited state molecule, as discussed in section 2.3.

Time-resolved experiments on molecules involve creating a molecular wavepacket that evolves depending on the coherent superpositions of molecular eigenstates that are populated by an excitation pulse of light. In this thesis, this wavepacket is subsequently probed by photoionisation. Although this is far from the only probing method in time-resolved

measurements, it does have great benefits compared to other methods, like transient absorption spectroscopy. Particularly, the probing step in TRPES can in principle probe any electronic states involved in the reaction, as there are no *dark states* to transition into a continuum.

Additionally, as discussed above, there are several ionizing sources that can provide different observables of the photochemical reaction. This thesis contains examples of XUV and soft X-ray sources, which provide high enough photon energies to ionize from any electronic state with a single photon. The X-ray probe is also site selective so one can monitor the binding energy for a single atom in the molecule. Ionizing laser sources also can achieve adequate temporal resolution for the femtosecond dynamics to be studied.

There are three main steps in the pump-probe method. Firstly, the start time (t_0) of the ‘pump’ pulse is incident on the sample, and the reaction is started. A coherent wavepacket in the excited state is produced. As discussed in section 2.2, this excitation is assumed to be a vertical transition faster than any proceeding nuclear dynamics.

For the second step, the wave packet evolves according to the energy phase factors contained within the superposition of the molecular eigenstates that were determined from eq. 2.5,

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_N A_N \exp(-iE_N t) \psi_N(\mathbf{r}, \mathbf{R}, t) \quad (2.15)$$

This wavefunction evolves as a function of time delay (t) depending on the electronic potential energy surfaces associated with the excited states (from eq. 2.6). In the case of nearly degenerate electronic states, the adiabatic assumptions in this wavepacket propagation break down.

Lastly, the probe pulse projects the wavepacket onto a specific final state, and for a photoionizing pulse, this is within the continuum, often assumed to be the first ionic state. The time dependence of an observed photoelectron signal is related to the transition dipole

moment, which contains properties of the probe pulse $\mathcal{E}(\omega)$, like in eq. 2.9⁴⁶,

$$\begin{aligned} S_f(t) &= |\langle \psi_f | \mathcal{E}(\omega) | \psi_i(t) \rangle|^2 \\ &= \left| \sum_n B_N \exp(-iE_N t) \right|^2, \end{aligned} \quad (2.16)$$

where expansion coefficients B_N contain the transition dipole matrix elements coupling each molecular eigenstate to the continuum,

$$B_N = A_N \langle \psi_f(\mathbf{r}, \mathbf{R}) | \mathcal{E}(\omega) | \psi_N(\mathbf{r}, \mathbf{R}, t) \rangle \quad (2.17)$$

To show the relationship between the wave packet dynamics and observed pump-probe signal, eq. 2.16 can be rewritten as

$$S_f(t) = 2 \sum_N \sum_{M \leq N} |B_N| |B_M| \cos((E_N - E_M)t + \alpha_{NM}) \quad (2.18)$$

This is the observable that shows that the signal is a coherent sum over all two-photon transition amplitudes in coefficients B_M and B_N and contains the interferences between all degenerate two-photon transitions. Modulations in the signal at frequencies $(E_N - E_M)$ correspond to spacings in the electronic surfaces, making them easily interpretable if eq. 2.18 is analyzed in the frequency domain after a Fourier transformation.

For the TRPES experiments in this thesis, the differential signal will be the electron kinetic energy as a function of pump-probe delay. To account for the two-photon contributions in pump-probe measurements, eq. 2.11 is easily modified to

$$E_0(\nu) + \omega_{pump} + \omega_{probe} = I_p^0 + E_{ion}(\nu) + E_{kin}^{e-}, \quad (2.19)$$

where, I_p^0 denotes the first ionization potential, from the Koopman's theorem formulation in eq. 2.10.

Some assumptions can be made regarding the rovibrational energies in the initial ground state ($E_0(\nu)$) and of the ion ($E_{ion}(\nu)$). Firstly, the experiments in this thesis were conducted with a supersonic molecular gas jet that is expected to cool through adiabatic expansion, so the thermal rovibrational contributions to the initial state are assumed negligible ($E_0(\nu) \approx 0$ eV)^{47,48}. Secondly, for probing the higher-lying electronic states, like the Rydberg manifolds described in section 4.2.1, we apply the $\Delta\nu = 0$ propensity, where we effectively couple to the ground ionic states and no rovibrational energy is carried by the ion, a generally good approximation in photoionisation of high-lying molecular Rydberg states^{49,50,51}

Also, as we wish to monitor the energy of the excited orbital, we assume the energy of the pump was deposited into this orbital, and maintain Koopman’s theorem is still valid: $I'_p = I_p^0 + \omega_{pump}$. With all these assumptions the measured kinetic energy in the pump-probe scheme is identical to eq. 2.11.

2.5 Experimental schemes

For photoelectron spectroscopy, two different detection techniques can be used. An experiment where the measured signal contains information of the the population of a single final state populated by the probe pulse is called *differential* spectroscopy. For TRPES, this final state is the ionization continuum. In these measurements the electron kinetic energy is resolved as a function of pump-probe delay. This is the primary technique for this thesis.

Otherwise, an *integration* measurement is where the measured signal is proportional to the total population in all final states. The observable in these measurements cannot distinguish a single final state, but rather integrates over all final states populated by the probe pulse. Examples of this technique are time-resolved fluorescence or photoion-yields. The experiment in section 3.5 was analyzed this way for time-resolved near-edge x-ray absorption spectroscopy, where the total Auger-Meitner electron yield was measured as a

function of photon energy and pump-probe delay.

Chapter 3

Experimental methods

This chapter discusses the experimental techniques used to study the nuclear and electronic structure of isolated molecular systems, both for static and time-resolved measurements. In this chapter, we will begin by describing the principles Free Electron Lasers (FELs), with special emphasis on comparing the different modes of operation that were used for work in this thesis; SASE versus seeded. Secondly, we will discuss the spectroscopic assemblies for photoparticle measurements, specifically those of magnetic bottle electron time-of-flight spectrometers (MBES) and reaction microscopes. Lastly, we will elaborate on the analysis techniques for experiments with certain FELs. We will place particular emphasis on using detector correlations and regression models to improve spectral resolutions from noisy sources, an imperative for the next generation superconducting high-repetition rate FELs.

3.1 Free-Electron Lasers

Studies in femtochemistry have been greatly advanced with the use of X-ray Free-Electron Lasers (XFELs). XFELs are light sources with properties comparable to conventional ultra-fast lasers, as they produce monochromatic, polarized, and collimated light beams⁵³. They can also generate sub-femtosecond pulses, making them suitable for pump-probe experi-

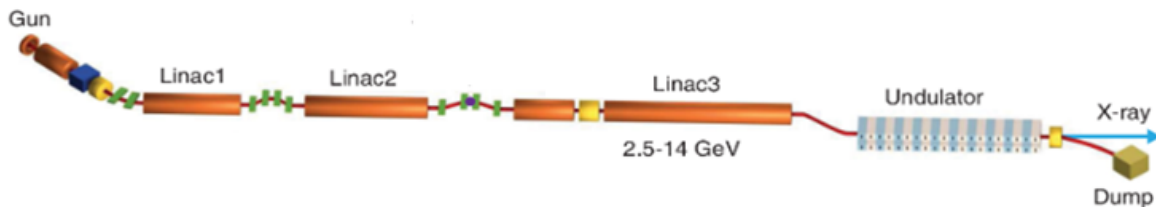


Figure 3.1: *Linac Coherent Light Source to illustrate main components of a high-gain X-ray free-electron laser. 1) Electron gun generating high charge electron bunches. 2) Three stage linear accelerators, and 3) the undulator and the electron dump.*⁵²

ments. However, unlike conventional lasers, they can generate these intense pulses in the extreme ultraviolet (XUV) and X-ray regimes.

With these properties, they enable measurements in gas phase photochemistry that are challenging to perform with smaller laser sources. For example, their high intensities can drive multiphoton ionization that can access very high charge states in atoms and molecules^{45,43}. Additionally, their tunable X-ray energies are valuable for site-selective investigations, allowing absorption at a single atom that has a unique absorption cross-section within a large molecule²². The layout of a free-electron laser is illustrated in fig. 3.1, using the Linac Coherent Light Source (LCLS) as an example⁵². The XFEL consists of four primary sections: the electron gun, which produces electron bunches in the pico- to nanocoulomb range; a three-section linear accelerator that accelerates electrons to relativistic speeds at GeV energies; the undulator, responsible for generating X-ray radiation; and the electron dump, which separates the X-ray pulses from the electron bunches.

3.1.1 Undulator Radiation

The high energy photons are generated via undulator radiation. An undulator is an array of alternating north and south magnetic poles that are all equally spaced by an undulator period, λ_u , typically a few centimeters, as shown in the top panel of fig. 3.2. This array generates a sinusoidally varying magnetic field in the direction transverse to the electron propagation.

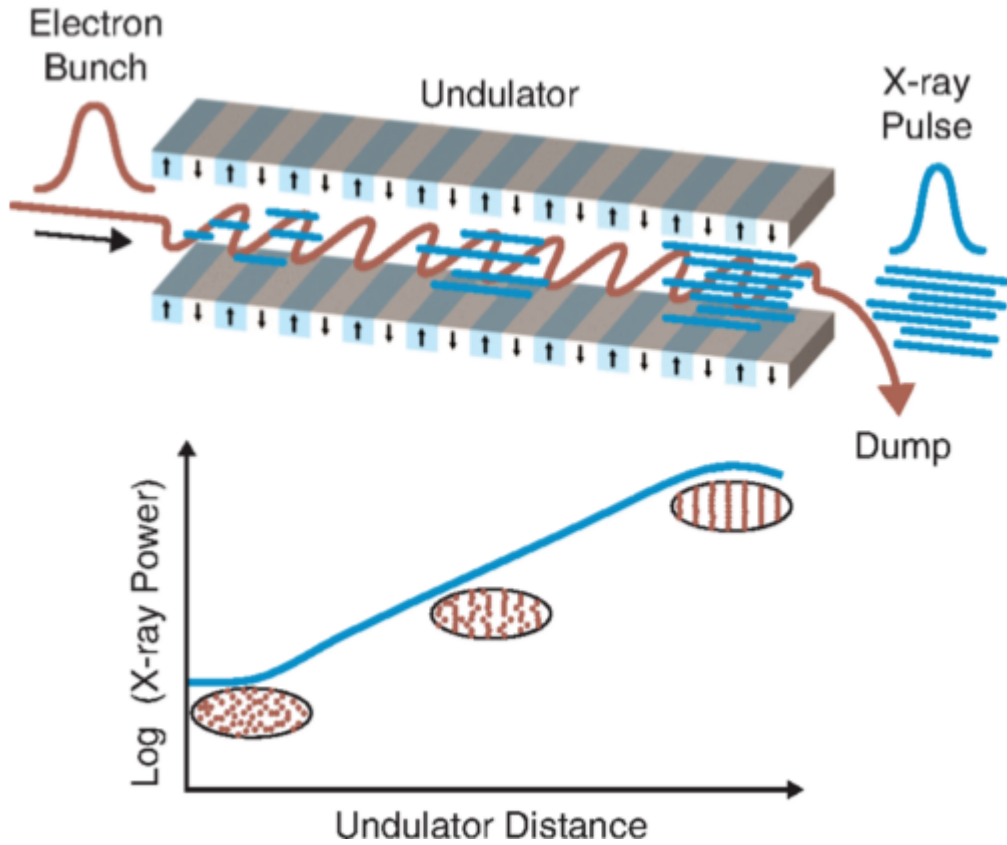


Figure 3.2: Undulator schematic. Top: the alternating magnetic poles and the transverse oscillations of the electrons in the corresponding periodic magnetic field. Bottom: Exponential increase of the X-ray pulse power and the microbunching of the electron that occur along the undulator length until saturation.⁵²

For all free electron lasers, electrons ejected from a cathode are accelerated to several GeV energies in a linear accelerator prior to being injected into the undulator. As these accelerated electrons are sent down the undulator they experience a sinusoidal Lorentz force which induces motion transverse to their propagation direction. In a frame that moves with the electron, the motion appears as a transverse harmonic oscillator, and they emit radiation with a frequency that equates to their oscillator angular frequency.

However, in the lab frame, this emitted radiation is Lorentz contracted due to the high-speed of the electron rest frame, enabling short wavelength undulator X-ray radiation. The radiated wavelength on the axis of electron propagation can be written as

$$\lambda_l = \frac{\lambda_u}{2\gamma^2} \left(1 + \frac{K^2}{2} \right), \quad (3.1)$$

where γ is the electron energy in units of its rest energy ($m_e c^2$). The dimensionless quantity $K = (eB_0\lambda_u)/(2\pi m_e c)$ is called the undulator parameter. Here, m_e and e are the mass and charge of the electron, respectively., B_0 is the field strength at the center of the undulator dipole magnets, typically around 1 Tesla. Ideally the undulator spacing and field strengths are adjusted such that undulator radiation power for the wavelength of interest is optimized.

The radiated power can be derived from the well-known Larmour formula⁵⁴,

$$P = \frac{e^2 c \gamma K^2}{12\pi\epsilon_0 \lambda_u \left(1 + \frac{K^2}{2} \right)}. \quad (3.2)$$

Here ϵ_0 is the vacuum permittivity. The radiation emitted from the free electrons in the undulator is incoherent by nature and the intensity will only scale linearly with the total number of electrons (N), $I \propto NI_0$, where I_0 is the radiation intensity of a single electron. These pulses emitted from undulators are fairly weak and have a large temporal width.

However, the geometry of the linear assembly of undulators in FEL enables much higher pulse energies using the principle of electron *microbunching*.

3.1.2 Microbunching

Microbunching is the process of concentrating electrons into very narrow slices within the undulator. This process occurs because the emitted radiation and the neighboring electrons interact with each other within the undulator.

As both the electromagnetic wave and the relativistic electrons have sinusoidal spatial profile, there will be places where the electron bunch gains or loses energy to the electromagnetic field depending on whether the electron velocity points parallel or perpendicular to the field polarization. This process causes the radiation to modulate the trajectory of the electrons, and they clump together to form these microbunches. The electrons within these microbunches will begin to radiate coherently.

Furthermore, in the radiating process, the light pulses will slip ahead of the electron bunch by one wavelength per undulator period. This *slippage* assures that the electrons will interact with the pulses of electromagnetic waves throughout the entirety of the undulator, causing further microbunching, and the radiation gain will increase exponentially⁵⁵. Once the bunch period is the same as the radiation wavelength, this process saturates, as shown in the bottom panel of fig. 3.2.

This is similar to a traditional quantum laser, which has a gain medium that provides amplification to the stimulated radiation (but the electrons associated with that gain medium are bound). In FELs, the electron bunches in the undulator act as the gain medium to the emitted X-ray radiation.

The metrics that relate the efficiency in the amplification process are that of the gain length (l_g) and the power gain-length (L_g), given as,

$$l_g = \frac{\lambda_w}{4\pi\rho} \tag{3.3}$$

$$L_g = \frac{l_g}{\sqrt{3}}. \tag{3.4}$$

The power gain length is defined as the distance into the undulator where the radiation power grows by 2.72. The expression for the gain length in eq. 3.3 shows that the relationship of the amplification process to parameters of the undulator and both electron and x-ray beams through the pierce parameter⁵⁶,

$$\rho = \left(\frac{1}{8\pi} \left(\frac{KJJ}{1 + \frac{K^2}{2}} \right)^2 \frac{\gamma\lambda_r^2}{2\pi\sigma_x^2} \right)^{1/3}. \quad (3.5)$$

Typcal values for ρ are around 10^3 . Here, I is the electron beam current. The Alfven current limit, $I_A \approx 17kA$ corresponds to the current value at which the beam's self-magnetic field is strong enough to reverse the direction of the electron trajectories at the outer edge of the electron beam⁵⁷. Thhe root mean square transverse size of the gaussian electron beam is σ_x , while $JJ = (J_0(\xi) - J_1(\xi))$ is a parameter depending on undulator parameters with J_0 and J_1 being Bessel functions of the first kind, and $\xi = (K^2/(4 + 2K^2))$.

The radiated power at saturation can be formulated with this pierce parameter and the power in the electron beam.

$$P_{\text{sat}} \approx \rho P_e = \rho \frac{\gamma m_e c^2 I}{e}. \quad (3.6)$$

This expression shows that the relationship between X-ray pulse power delivered monotonically increases with K and γ .

The slippage in the FEL undulators is also the mechanism that makes the pulses from an FEL so short in time. In principle, if the x-ray amplification was localized to a single bunch, the pulse duration could be as low as the time for the light to travel across that single gain slippage length, on the order of 1 fs⁵⁸. Due to the exponential scaling of x-ray power in the undulator, most of the radiation is produced in the final gain length.

Several assumptions were made for the process of making these high intensity, ultra-short duration x-ray pulses. Non-ideal conditions, such as changes in beam steering can significantly degrade these qualities.

3.1.3 SASE and seeded FELs

For the studies in this thesis, three different FELs at different facilities were used. They are SLACs Linac Coherent Lightsource (SLAC-LCLS) at Stanford, European XFEL in Hamburg, and FERMI at Elettra Sincrotrone Trieste.

The amplification processes for these different FELs are similar, however the methods of initiating the amplification are different, and fall into two categories; Self-Amplified Spontaneous Emission (SASE) and seeded modes. The underlying difference between SASE and seeded operations lies in how the electron beam modulation to induce microbunching occurs. These two modes result in distinct FEL pulse properties and experimental requirements.

SASE

In the *SASE* mode, the FEL process can be interpreted as starting from shot noise²⁵. There will be some inherent, albeit unstructured, modulations in the initial electron beam. These stochastic modulations will have some low emittance. This emittance resembles white noise and will have some components within the FEL bandwidth and will initiate the lasing process. The undulators are tuned to optimize the max fluence for the desired soft-xray wavelength, and so this technique provides intense pulses of high energy photons.

However, the noisy startup process causes several different wavelengths to be radiated within the pulse and have random phase shifts between them. This leads to a stochastic frequency spectrum with several narrowband, high-intensity SASE spikes. The distribution of these spikes will change randomly on a shot-to-shot basis. Additionally, these random phase shifts lead to a short coherence time within the pulse, and the pulse energy fluctuations tend to be very large. Figure 3.3 demonstrates the strong intensity variation in the SASE modes on a single shot basis, a property called *jitter*.

All these stochastic properties of the SASE pulses can degrade the spectral quality of photoelectron or X-ray absorption measurements when averaged over several shots. Thus, when operating in SASE mode it is important to have single-shot diagnostics of the spectrum

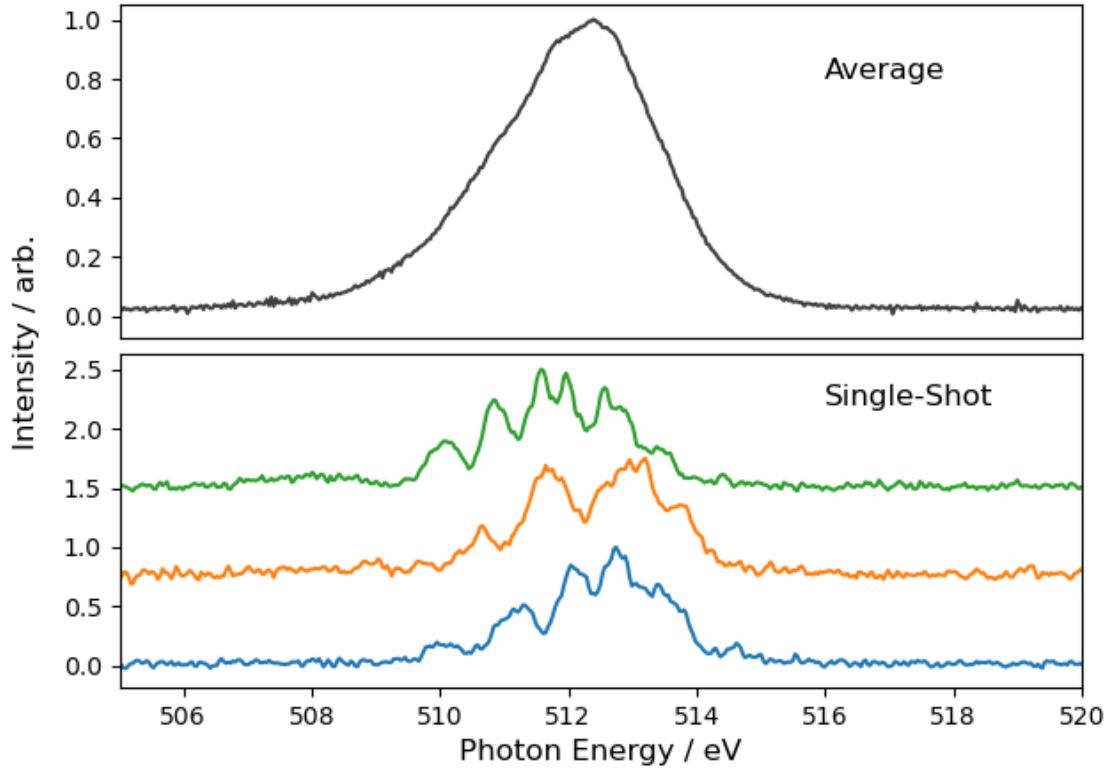


Figure 3.3: *Averaged and single shot spectra of individual SASE pulses with a central photon energy of 410 eV. Several high intensity sub-eV SASE spikes are apparent in the single shot traces.*

to account broad bandwidth in SASE parameters.

Seeded

If instead the electron bunch is modulated by a high coherent optical laser prior to the undulators, the startup process would be induced by a single, stable mode. Thus, microbunching will occur quickly and the FEL radiation will be spatially and temporally coherent. Then fluctuations would be minimized.

At the FERMI FEL in Elettra, the seeding process is done via the High-Gain Harmonic Generation (HGHE) process^{59,60}. Here a harmonic of a coherent laser source in the deep ultraviolet region acts as a seed and modulates the electrons, as shown in fig. 3.4. Firstly, this optical seed beam and the electron beam are sent through a short undulator called the modulator. The modulator shapes the energy of the electron beam sinusoidally. Secondly, the electron bunch moves through a magnetic chicane that converts the energy modulation into charge density modulation, generating narrowly spaced electron macrobunches. Finally, the electron bunch is sent into a longer undulator, called the radiator, which has undulator parameters tuned to a higher harmonic of the seeded laser such that density-modulated beam produces FEL radiation at this wavelength.

Because the FEL process in seeded operation is synchronized to a coherent source the jitter is negligible, and the pulses have narrow bandwidth, as shown in fig. 3.5. However, the seeded mode often limits photon energies to the XUV region as the lasing wavelength can only be a few harmonic orders of the seed laser itself, which is typically done in the deep UV wavelengths, as these sources provide the fluence to initially modulate the electron beam.

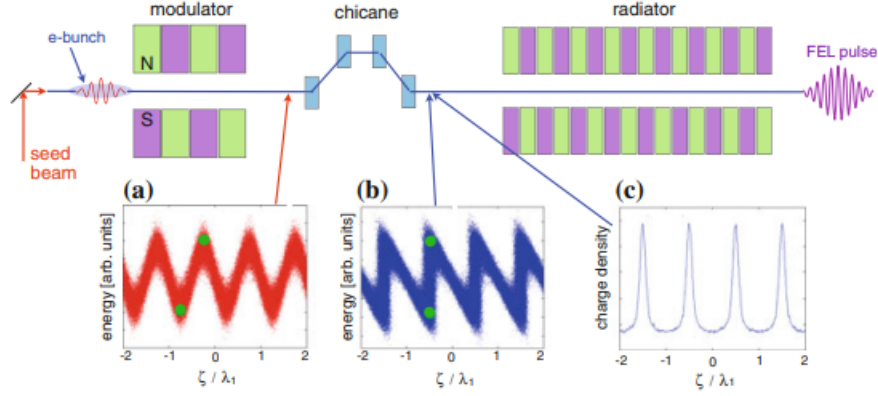


Figure 3.4: Schematic of seeding process via high-gain harmonic generation. The top graph shows the three main components: the modulator wherein the seed beam and electron bunch interact, the chicane and the main radiator where the FEL radiation is generated. Longitudinal phase space distributions of the electron energy before and after charge density modulation from the magnetic chicane are shown in panels **a** and **b**, respectively. Energy and charge density are shown as functions of internal bunch coordinate ξ , which relates the phase relation of the electron and the electromagnetic wave.⁵⁵

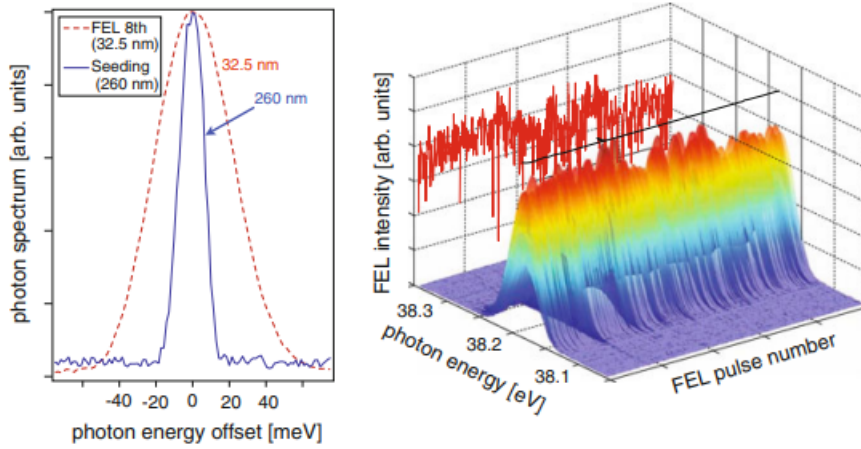


Figure 3.5: Spectral properties of HGHG seeded operation. Left: seed laser and FEL at the 8th harmonic showing narrow spectral width. Right: Single shot spectra showing negligible variations in the central photon energy and stable pulse intensity.⁵⁹

3.2 Photoelectron and photoion measurements

Ionizing radiation from these FELs is used to probe gas phase molecular systems. Information about molecular electronic and nuclear structure, and the changes they undergo upon excitation, can be extracted from photoparticle kinetic energies, angular distributions, and momentum correlations between several particles. The spectroscopic techniques used in this thesis fall into two categories. First are photoelectron spectroscopies, in which the goal is to study the time-evolving electronic structure of UV excited molecules. The electron spectrometer assembly used in this thesis is the magnetic bottle electron spectrometer (MBES). Secondly is photoion coincidence spectroscopies. In this case, we study fragmentation of highly ionized molecules employing cold target recoil ion momentum spectroscopy (COLTRIMS).

3.2.1 Magnetic bottle electron spectrometers

In time-resolved photoelectron spectroscopy, the aim is to track changes in the electronic structure of a molecule upon photoexcitation. In the most basic formulation, extracting the kinetic energies of photoelectrons or Auger-Meitner electrons can elucidate the changing electronic dynamics as the molecule relaxes from photoexcited states to the ground state. For these measurements involving complex molecules, good energy resolution is imperative, and when performing these measurements with FELs, where shot-repetition rates are currently low and acquisition times are short, high collection efficiency is also a necessity. The magnetic bottle electron time-of-flight spectrometer is particularly suited for these applications^{61,62,63}.

In a standard magnetic bottle spectrometer, electrons generated at a localized laser-sample interaction point are directed to the detector through by a magnetic fields, via the Lorentz force, as shown in fig. 3.6. The spectrometer includes an extended flight tube (approximately 2 meters long) housed within a magnetic solenoid that provides the uniform

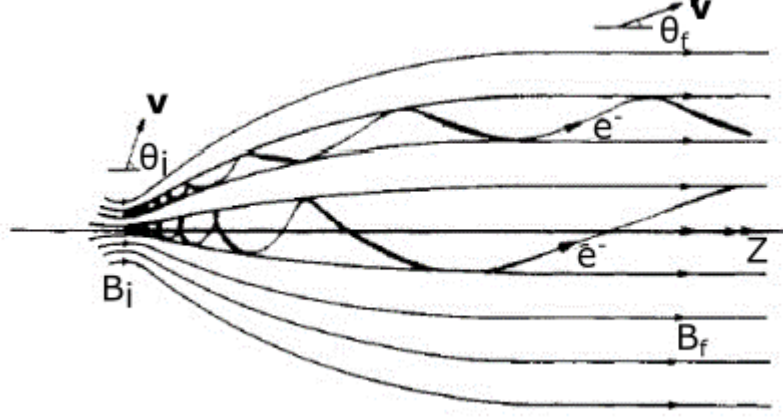


Figure 3.6: *Magnetic bottle electron spectrometer field diagram showing the slow variation from initial strong field B_i to the final strong field, B_f . Helical motion of the electrons emitted at different initial angles and the parallelization of their final trajectories.*⁶¹

magnetic field.

To have 4π acceptance and be spatially selective in the interaction region, a second permanent magnet often sits opposite of the flight tube, providing stronger flux that guides electrons that were emitted antiparallel to the flight tube axis (see figure 1 in section 3.4 for a schematic). The electrons undergo periodic cyclotron motion with a frequency and radius of

$$\omega = \frac{eB}{m_e}, \quad (3.7)$$

$$r = v \sin(\omega_i)/\omega, \quad (3.8)$$

respectively. Here, B is the magnetic field strength, v is the magnitude of the initial electron velocity, and θ_i is the emission angle of the electron relative to the spectrometer axis. The magnitude of the electron's velocity is unchanged as it is only under the influence of the magnetic force. The angular momentum of the electron is

$$l = \frac{m_e^2 v^2 \sin^2(\omega_i)}{eB_i}. \quad (3.9)$$

So long as the magnetic field is adiabatic, such that it has negligible variation within a

single helical motion of the electron, the angular momentum of the electron is conserved⁶¹. This mechanism is key for the parallelization of the electron trajectory, the electron's velocity vector at the end of the tube will point parallel to the flight-tube axis.

$$v_{zf} = v \left(1 - \left(\frac{B_f}{B_i} \right) \sin^2(\omega_i) \right) \quad (3.10)$$

This parallelization enables the full 4π acceptance of the electrons with no strong extraction fields that would deteriorate the energy resolution

Additionally, as the energy resolution is proportional to the time of flight (TOF) via the relationship

$$\frac{\delta E}{E} = \frac{\delta TOF}{TOF} \quad (3.11)$$

, some magnetic bottles are equipped with a retarding lens assembly to slow the electrons from their initial velocities with a uniform electric field^{64,65,66}.

The two MBES described in this thesis are located at the Low-Density Matter (LDM) beam line at the FERMI FEL⁶⁷ and the Time-resolved AMO (TMO) at the LCLS-II FEL⁶⁸. They are similar in setup. Both have an approximately 2-meter-long flight tube and retardation plate stack. The two key differences are the detector schemes and permanent magnet steering.

As discussed later in this chapter, the experiments conducted at TMO wish to acquire a broad range of electron energies simultaneously, as in the case of photoelectron and Auger-Meitner electron covariance measurements^{69,70}. Therefore, the TMO MBES is equipped with a segmented anode detector that enables simultaneous modes of operation, where one can measure a certain electron energy range with high detection efficiency and a high resolution in another.

With the limited energies accessible with the XUV line at the FERMI FEL, this spatial discrimination with a segmented anode is unnecessary and thus we record with a single anode detector. Additionally, the MBES at TMO is equipped with a three-dimensional movable

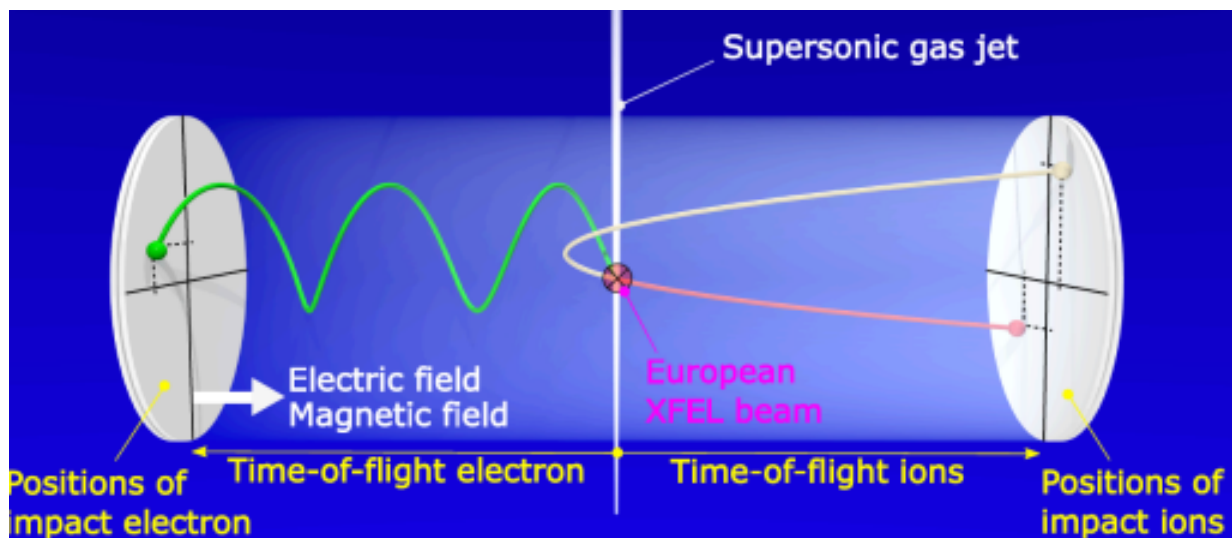


Figure 3.7: *COLTRIMS* schematic. Gas phase sample is introduced via a supersonic gas jet. The ion trajectories are traced in red while electron helical trajectories in green. Fragments are guided by a uniform electric field along the time-of-flight axis. Positions of charged particles are detected by an mcp stack coupled to a delay-line anode. Note that for the work in this thesis that focuses on high-fold ion-ion coincidence, no electrons were measured.⁷¹

magnet, while the FERMI MBES magnet is only adjustable parallel to the spectrometer axis.

With the similarities of these two MBES, more elaborate discussion is included in a paper in section 3.4 that details the performance of the TMO magnetic bottle spectrometer, including a discussion of its compatibility with photoelectron spectroscopy from a noisy SASE-FEL, and a modulation transmission function that is ubiquitous in magnetic bottles.

3.2.2 COLTRIMS

For experiments in which we want to observe nuclear dynamics within a molecule, we employ the COLd Target Recoil Ion Momentum Spectroscopy (COLTRIMS) method^{72,73}. This spectrometer type enables three-dimensional momentum resolved measurements in the center-of-mass frame of a photodissociation reaction. If this dissociation reaction occurs rapidly, with all fragments produced simultaneously without intermediate rotations, the

measured asymptotic momenta can provide information on the nuclear geometry⁷⁴.

It is necessary to perform these measurements in a coincidence mode, where particle detection on a time and position sensitive detector are correlated with each other to assure photofragmentation within a single shot truly comes from an isolated molecule at the interaction point. The kinetic energies and angular distributions of the photofragments from these events are then correlated with each other to gain an understanding of the photodissociation process. To probe structure and dynamics of neutral molecules with reasonable statistics, all of these coincidence procedures are best suited for very low background pressures and dilute molecular beam sample deliveries that are very cold and well collimated, minimizing the thermal distributions and capture the molecular geometry with minimum rotational or vibrational distributions. These conditions minimize the amount of false coincidence events (where particles from two different molecules are detected within a single shot) and provide good momentum resolution.

To generate the unidirectional electric field, a series of equally spaced electrodes (typically 50 thin plates with ~ 5 mm spacing) are connected in series by identical resistors (typically $1M\Omega$). High voltages of opposite polarity are applied to the two ends of the spectrometer, generating a uniform voltage drop across the spectrometer (typically ~ 150 V/cm). These fields are sufficient to guide highly energy ions to the detector, enabling the detection with recoil energies up to 70 eV emitted perpendicular to the spectrometer axis.

To achieve the cold molecular beam sample and very low target density, a supersonic gas jet device is ubiquitous for COLTRIMS assemblies. This includes very small nozzle (typically 10 s of μm in diameter) that holds very high backing pressures (several bar for samples seeded with helium). The gas jet is separated into four differential pumping stages that are separated by small skimmers (typically ~ 1 mm in diameter) that select only the central narrow slice of the molecular beam. Each section can reduce the pressure by two orders of magnitude. The gas jet is also equipped with a set of slits just before the interaction region that enables cutting the outer, warmer sections of the molecular

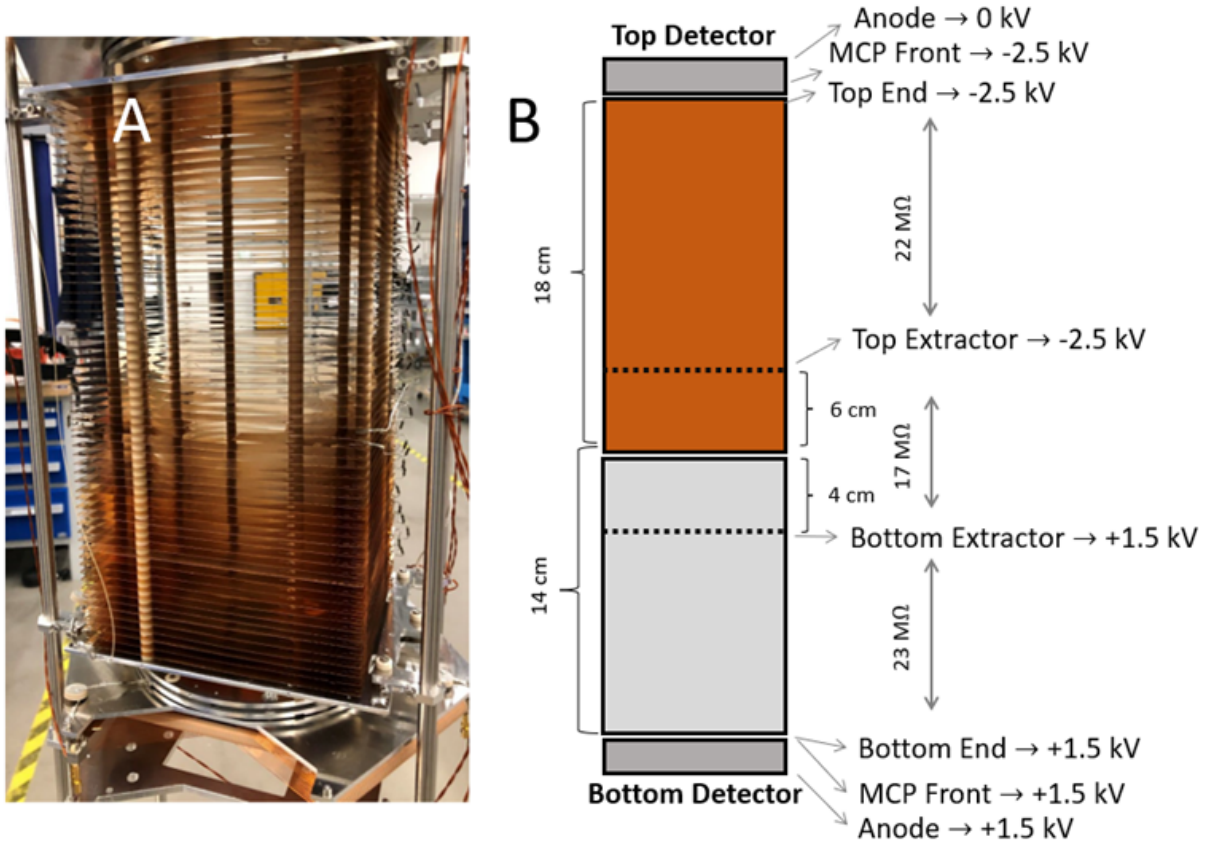


Figure 3.8: *Spectrometer design of SQS-REMI Instrument* **A)** *Photograph of spectrometer* **B)** *Schematic showing lengths of spectrometer segments and operating voltages.*

beam. The molecular beam is introduced to the main chamber with very low base pressures (typically around 10^{-11} Torr). With these vacuum levels and a dilute enough molecular beam sample in the interaction volume, the X-ray pulse could see as little as one molecule per shot, creating ideal conditions for ion coincidence measurements.

In usual COLTRIMS experiments, the three-dimensional momentum reconstruction for the photofragments is determined by a time and position sensitive detector. For the x - and y - directions perpendicular to the spectrometer axis, these values are recorded with a delay line anode. This anode consists of at least two wires wound reciprocating each other. Signal arrival times are measured at opposite ends of each wire, and the difference between their arrival times can be used to determine where the particle landed in the x and y positions with the simple formula

$$x = \frac{V}{2D}(t_1 - t_2), \quad (3.12)$$

where V is the signal speed transfer, D is the total length of the wire, and t_i is the arrival time of the electronic pulse to reach the individual end of the wire.

The time-of-flight, spectrometer voltage and length, and the position values are necessary to convert these values to momentum and analyze the photodissociation observables in the lab frame. With appropriate characterization of the molecular and X-ray beam interactions (such as the jet velocity and the beam interaction point coordinates), the center-of-mass momentum can be determined, as discussed in section 5.4.

In this thesis the COLTRIMS technique was employed for a measurement using Coulomb explosion imaging to distinguish different isomers with the chemical formula of C_7H_8 , toluene, cycloheptatriene, and 1,6-heptadiyne. For the analysis procedure of CEI, and the results of this experiment, see section 5.4.

3.3 Detector correlation analysis

As illustrated above, SASE XFEL sources have inherent instabilities in several key parameters on a shot-to-shot basis, including the inherent spectral jitter and fluctuating pulse energies. Additionally, the laser-FEL timing stability in pump-probe measurements degrades due in part to the SASE lasing mechanism, but also because of thermal instability, RF noise, and spatial drifting between the laser and FEL beams⁷⁵.

These problems can be mitigated by taking single-shot measurements that can encode a value for the shot-to-shot jitter and correlating them with the main observable of interest in the experiment. Using this correlation, one can correct for the jitter and improve the spectral resolution, and also account for noise in either detector. This procedure is like the classical ghost imaging technique⁷⁶.

In classical ghost imaging, a high-resolution image of an object is reconstructed by correlating information from two detectors that are illuminated from a split coherent beam. One is a spatially sensitive detector that does not contain any information of the object, but rather encodes the fluctuation of the probing light source. The second is a single-pixel detector that sits behind the object being studied.

This carries over to photoelectron spectroscopy with SASE FELs, a term called Frequency Domain Ghost-Imaging (FDGI) or Spooktroscopy^{77,78,79}. In this case one simultaneously measures a single-shot photoelectron and a photon energy spectrum. To reconstruct a photoelectron spectrum with improved resolution that would otherwise be degraded due to the noisy SASE probe, we solve for the spectral response function that maps the measured incident photon spectrum to the measured photoelectron kinetic energy spectrum.

In the single photon regime, this spectral response can be formulated as the partial absorption cross section, and the total electron yield can be written as the product between this cross-section and the photon spectrum integrated over all frequency components

$$b = \int d\omega A(\omega)\chi(\omega). \quad (3.13)$$

This can be represented as the over- or under-determined system of equations, $A\mathbf{x} = b$. Here A is the measured X-ray photon spectrum, represented as an $n \times m$ matrix, where n is the number of FEL shots and m is the number of energy bins in the spectrum. The matrix b represents the measured kinetic energy spectrum, represented as an $n \times p$ matrix, where p is the number of kinetic energy bins.

Many methods exist to solve this expression for the response function, $\mathbf{x}$, such as the Moore-Penrose pseudoinverse, however these solutions are inherently unstable⁸⁰. This means that small variations within the noise of either A or b can change the solution x drastically. Thus, it is preferable to impose physically meaningful constraints on this equation and solve for the x that minimizes the constrained equation

$$|Ax - b|_2^2 + \lambda_s |x|_1 + \text{Ind}_+(x) + \sum_{i=1}^2 \lambda_i |L_i x|_2^2. \quad (3.14)$$

Here λ_i are hyperparameters that weigh the degree of smoothing across either the photon or photoelectron energy axis, which is quantified by the Laplacian operator (L_i). Hyperparameter λ_s weighs the sparsity of the solution, quantified by the norm of the solution $|x|$. The indicator function, Ind_+ , which is 0 when the argument is non-negative and infinity otherwise, constrains the solution to be a positive value.

From the solution x , the correlation of the reference photon and photoelectron energy measurements become apparent, as clear dispersion lines are seen and can be distinguished from noisy features, as shown in fig. 3.9.

To represent the photoelectron spectrum as a well resolved, one-dimensional spectrum we can correct for this dispersion and integrate over the photon energies. Although introducing the hyperparameters to the system of equations significantly improves the data quality, and they are robust over several orders of magnitude, they can superficially affect the resolution of the measurement if selected inappropriately. Several methods exist to verify the appropriate selection of hyperparameters for a given problem. In the reconstructions presented

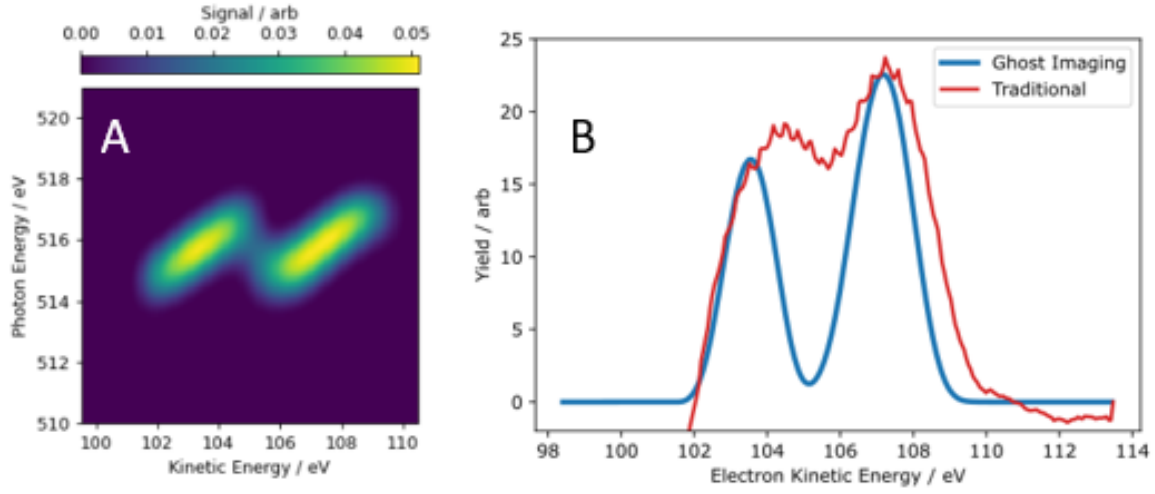


Figure 3.9: Spectral response of nitrous oxide using frequency domain ghost imaging to distinguish the central-terminal splitting in the binding energies of nitrogen sites. A) Two-dimensional representation showing dispersion of the electron kinetic energy spectra against the measured photon energy spectra. B) Accounting for the dispersion and projecting over all photon energies. Comparing ghost imaging reconstruction of this spectra against the traditional measurement that is unable to resolve the splitting due to the large single shot jitter in the central photon energy.

in this chapter, the hyperparameters were selected via the L-curve method, where a log-log parametric plot for the norms of the solution residuals and regularization operation is analyzed^{81,82,83,84}. With this visualization one can see a vertical and horizontal asymptote that corresponds to regions of overfitting, as shown in panel A of fig. 3.10 and overregularization (either oversmoothing or oversparsification) like in panel C. A good compromise is seen at the sharp bend in this L-curve where the curvature is maximized, like in panel B.

The Spooktroscopy method can be extended to the time-domain, where one can reconstruct the pump-probe delay signal that is degraded by large temporal jitters associated with unseeded operations. This is particularly beneficial for detector correlations that operate at different acquisition rates. In this case, a detector is unable to operate at the full repetition rate of the FEL, and thus needs to average over several shots. Within this averaging window several pump-probe jitter values would be sampled but could not be differentiated, and hence the temporal resolution of the signal would be degraded as we average over several delays. By applying the same logic of the frequency domain ghost imaging to this time-domain problem, one can reconstruct the pump-probe signal with such improved resolution, that it is as if the slow detector is not integrating at all.

3.4 Design and performance of a magnetic bottle electron spectrometer for high-energy photoelectron spectroscopy

This section includes work discussing the developments of the magnetic bottle electron spectrometer coupled to the TMO endstation at LCLS⁸⁵. At the time of writing this thesis, this manuscript is in review.

This manuscript discusses the instrument design and performance. We demonstrate the resolution, collection efficiency, and spatial selectivity. Particular topics, like employing

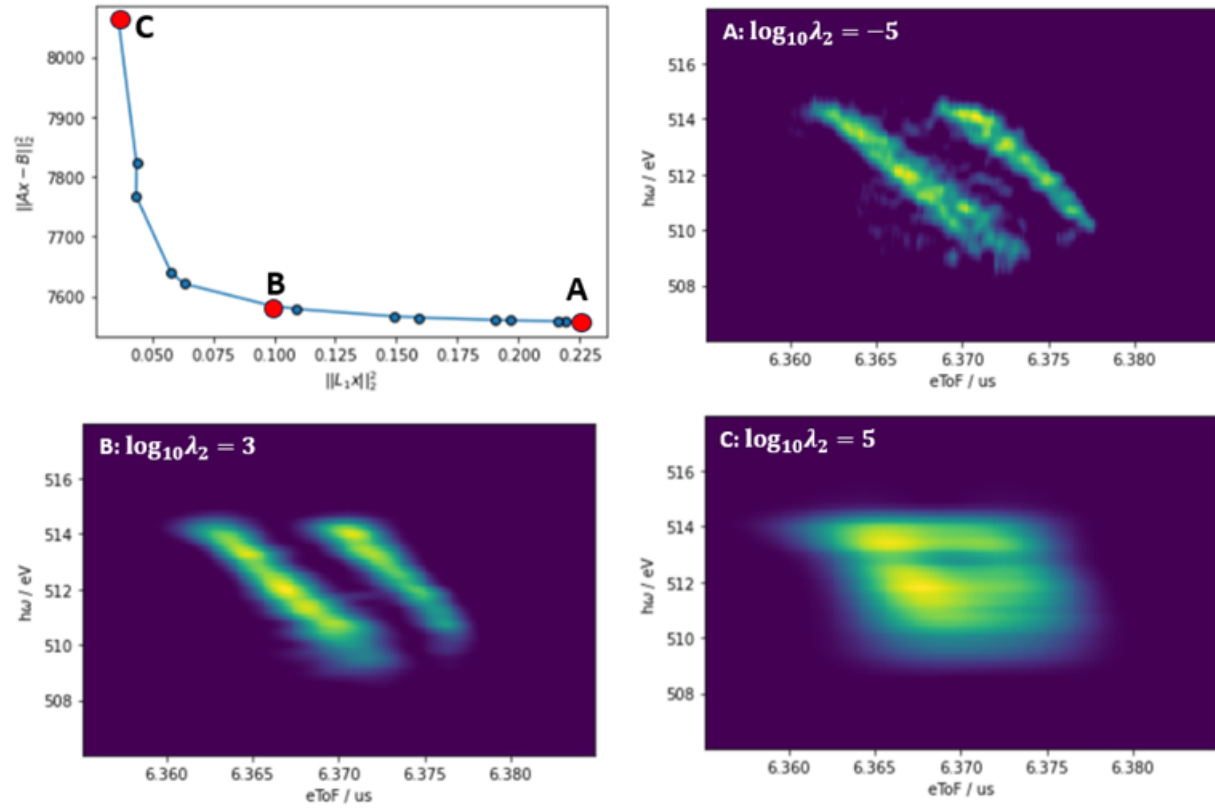


Figure 3.10: Ghost imaging reconstructions of nitrogen photoelectrons in nitrous oxide with different hyperparameters. Upper left panel shows the L-curve which is a log-log plot of the solution residual against the L-2 norm of the solutions Laplacian. Changing this hyperparameter varies the degree of smoothing along the horizontal axis. At the upper corner of the L-curve, the hyperparameter λ_2 is very small and the solution overfits to the data, as shown as the noisy features in **A**. At the bottom right of the L-curve, λ_2 is very large and the solution is drastically oversmoothed, as shown in panel **C**. At the corner of the L-curve, a good compromise between these is achieved, as shown in panel **B**.

frequency-domain ghost imaging for photoelectron spectroscopy and addressing a common periodic modulations in electron detection efficiency, are explained in much more detail than in section 3.2.1.

Coauthor Jordan T. O’Neal developed the algorithm discussed in section IV⁸⁶, and generated figures 11 and performed analysis on a para-aminophenol experiment, with results in figure 12. Coauthor Jun Wang performed the electron-electron covariance analysis for the results in figure 5.

I helped with modifications to spectrometer and coupling the chamber to the LCLS beamline. I helped with operations during the commissioning beamtime, along with the rest of the TMO team. I analyzed the data, wrote the draft, prepared the manuscript with feedback from all coauthors, and submitted for publication.

Design and Performance of a Magnetic Bottle Electron Spectrometer for High-Energy Photoelectron Spectroscopy

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(Dated: 13 April 2024)

We describe the design and performance of a magnetic bottle electron spectrometer (MBES) for high-energy electron spectroscopy. Our design features a ~ 2 m long electron drift tube and electrostatic retardation lens, achieving sub-electronvolt (eV) electron kinetic energy resolution for high energy (several hundred eV) electrons with close to 4π collection efficiency. A segmented anode electron detector enables the simultaneous collection of photoelectron spectra in high resolution and high collection efficiency modes. This versatile instrument is installed at the TMO endstation at the LCLS x-ray free-electron laser (XFEL). In this paper, we demonstrate its high resolution, collection efficiency and spatial selectivity in measurements where it is coupled to an XFEL source. These combined characteristics are designed to enable high-resolution time-resolved measurements using x-ray photoelectron, absorption, and Auger-Meitner spectroscopy. We also describe the pervasive artifact in MBES time-of-flight spectra that arises from a periodic modulation in electron detection efficiency, and present a robust analysis procedure for its removal.

I. INTRODUCTION

Electron spectroscopy is a powerful tool for probing the electronic and molecular structure of gaseous and condensed phase systems. When used in combination with ultrashort light pulses, the technique offers a route to tracking ultra-fast electronic and nuclear dynamics. Time-resolved photoelectron spectroscopy (TRPES) of valence electrons is an established technique for probing photo-initiated molecular dynamics on the femtosecond timescale [1–4]. The binding energies of core orbitals can be particularly sensitive to the local chemical environment, so the nascent ability to time-resolve small binding energy shifts in inner shells promises to be a useful tool for tracking dynamics in molecular systems [5–9]. Resonant x-ray absorption measured using Auger-Meitner spectroscopy also offers a powerful probe of the transient localized valence electron density in molecules [10–12].

A magnetic bottle electron spectrometer (MBES) combines a strong (~ 1 T), inhomogeneous magnetic field at the interaction point with a weaker (~ 1.5 mT) uniform magnetic field through a long drift region (or flight tube). This configuration achieves a high-collection efficiency for electrons while maintaining a good kinetic energy resolution. Electrons emitted in different directions from the interaction point are guided *via* the Lorentz force along the magnetic field lines and into the flight tube, where they undergo betatron oscillations about the flight tube axis as they travel towards the detector. The original MBES design afforded 2π solid angle collection volume, by collecting all electrons emitted in the hemisphere directed toward the flight tube [13, 14]. Later developments increased

the collection efficiency to 4π by exploiting the magnetic mirror effect [15]. Some designs [16–18] make use of an electrostatic retardation lens to reduce the electron velocity through the flight tube and so increase kinetic energy resolution. The high detection efficiency of the MBES is particularly advantageous for electron-electron coincidence or covariance measurements [19–22], for which the signal-to-noise is critically dependent on collection efficiency [23]. Finally, MBES has proven particularly useful for electron spectroscopy at x-ray free-electron lasers (XFELs) [11, 20, 22, 24, 25].

In this work, we describe the design and performance of a MBES, which is installed at the time-resolved atomic, molecular and optical physics (TMO) instrument at the Linac Coherent Light Source (LCLS) [26]. Our design features a ~ 2 m long flight tube, an electrostatic retardation lens and a segmented anode electron detector, which enables the simultaneous acquisition of electron spectra in two different collection modes: high resolution and high collection efficiency. We show that the high collection efficiency enables covariance mapping of photoelectron/Auger-Meitner electron emission in the core ionization of nitrous oxide. We employ spectral domain ghost imaging [27–29] in combination with the single-shot spectral diagnostics available at the beamline to isolate the resolution of our spectrometer from the inherent spectral width associated with a self-amplified spontaneous emission (SASE) XFEL. We achieve an electron energy resolution of $\frac{\delta E}{E} \sim 1/100$.

II. INSTRUMENT DESIGN

A schematic of the MBES is shown in Fig. 1. The inhomogeneous magnetic field at the interaction point is generated by a nickel-coated neodymium permanent magnet. A soft iron cone is mounted on the permanent magnet and acts as a magnetic shunt to focus the magnetic field lines at the interaction point. The permanent magnet is mounted to a remotely controlled three-axis manipulator to facilitate spectrometer alignment. The tip of the iron cone sits 6 mm opposite a copper nose cone, which is mounted on a 1.95 m long drift tube. The interaction point sits directly between the tip of the iron cone and the tip of the copper nose cone. The key elements of our design are modeled using the SIMION package to simulate the trajectories of electrons through the MBES. These simulations are detailed throughout the results of the manuscript.

The drift tube has an outer diameter of 76 mm and is wrapped by kapton-insulated, 22 AWG wire, which acts as an in-vacuum solenoid, with ~ 1.2 turns/mm. To achieve a uniform magnetic field of ~ 1.5 mT in the drift tube, a current of ~ 1 A is applied to the coil. The drift tube is mounted inside a DN160 CF stainless-steel tube, which is wrapped in a sleeve of high-magnetic-permeability metal to mitigate the effects of external magnetic fields on electrons traveling through the tube.

There is an electrostatic lens in the drift tube to create a decelerating electric field to slow the electrons, which increases their time-of-flight, improving the energy resolution of the spectrometer. The position of the lens was chosen such that the magnetic field lines created by the combined fields of the permanent magnet and solenoid are parallel to the electric field lines of the lens. The lens begins ~ 183 mm from the interaction point and consists of two pairs of three electrostatic lens plates with ~ 6.1 mm spacing, separated by ~ 30 mm. Each set of three plates is electrically connected and a retarding effect is produced on the electrons by applying a potential between the two triplets.

Electrons are detected at the end of the drift tube by a 40 mm diameter micro-channel plate (MCP) detector coupled to a conical anode (Surface Concept GmbH). The anode is segmented into two concentric sections of 3 mm and 40 mm diameter, with a 1 mm spacing ring between them. In operation, ~ 1.8 kV is applied across the chevron MCP stack with a further ~ 300 volts to the anode. The voltages on the two anodes are decoupled from the high voltage source and amplified (Ortec 9306, 1 GHz preamplifier), digitized with 168 picosecond precision, and read into our data recording system.

The segmented anode design was chosen to enable the simultaneous collection of spectra with high energy resolution (lower collection efficiency) and high collection efficiency (lower energy resolution). In a MBES, the time-of-flight distribution of monochromatic electrons features a characteristic long tail, consisting of electrons emitted perpendicular to the time-of-flight axis but still directed down the flight tube by the inhomogeneous magnetic field [13]. In simulation, we find that the electrons with longer time-of-flight impinge on the detector at larger radii (i.e. further from the center of the detector), as shown in Fig. 2 A-C. The segmented anode enables the

exclusion of this long time-of-flight tail by selectively detecting electrons which land close to the center of the detector. For measurements requiring higher detection efficiency, it is possible to also include electrons detected on the outer anode. Inclusion of these electrons causes a broadening of the peaks in time-of-flight, to the detriment of the kinetic energy resolution.

III. INSTRUMENT PERFORMANCE

The MBES is currently installed in the LAMP [30] chamber at the TMO endstation [26] at the Linac Coherent Light Source (LCLS) XFEL. In this work we characterize the performance of the MBES for x-ray photoelectron spectroscopy with an XFEL source, making use of SASE pulses with a duration of < 50 fs and a median pulse energy of approximately $50 \mu\text{J}$. X-rays were focused to a $\sim 1 \mu\text{m}$ diameter at the interaction point of the MBES using a pair of Kirkpatrick-Baez mirrors [31]. The base pressure of the chamber housing the MBES was below 2×10^{-9} Torr and the sample gas was introduced to the interaction point using an effusive gas needle. The TMO endstation also features a transmissive Fresnel zone plate-based x-ray spectrometer which enables a shot-to-shot characterization of the incoming x-ray spectrum [32]. This measured x-ray spectrum is used for the spectral-domain ghost imaging analysis described in section III F.

A. Segmented Anode

As described in section II, the MBES features a segmented anode to discriminate the time-of-flight spectrum based on the position of electron impact on the MCP detector. The central part of the anode has a diameter of 3 mm, and is separated from the outer anode (diameter 40 mm) by a ring of 1 mm thickness. Panels A–C in Fig. 2 illustrate the motivation for this design. Panels A and B show simulation results for 10,000 electrons sampled from an isotropic distribution of emission angles, with an initial kinetic energy of 812 eV and 400 V retardation applied to the electrostatic lens. The coupling between electron time-of-flight and arrival position at the detector plane is shown in Fig. 2 A. The simulations show that electrons contributing to the prompt peak in the time-of-flight distribution, which are initially emitted along the axis of the flight tube, impinge close to the center of the detector. The slower electrons, which produce the tail in the time-of-flight distribution and are emitted with a significant velocity component perpendicular to the time-of-flight axis, impinge on the detector at larger radii. This effect is made clear in Fig. 2 B, which shows the simulated time-of-flight spectrum for all electrons (black dotted line), and only those which arrive within a 1.5 mm of the detector center (blue line). In panel C we explore the coupling between time-of-flight and detector position for different kinetic energies and find that it is a general effect: electrons which impinge at larger radii have a longer time-of-flight. The retardation voltage for the simulations in panel C was 100 V but we have verified that

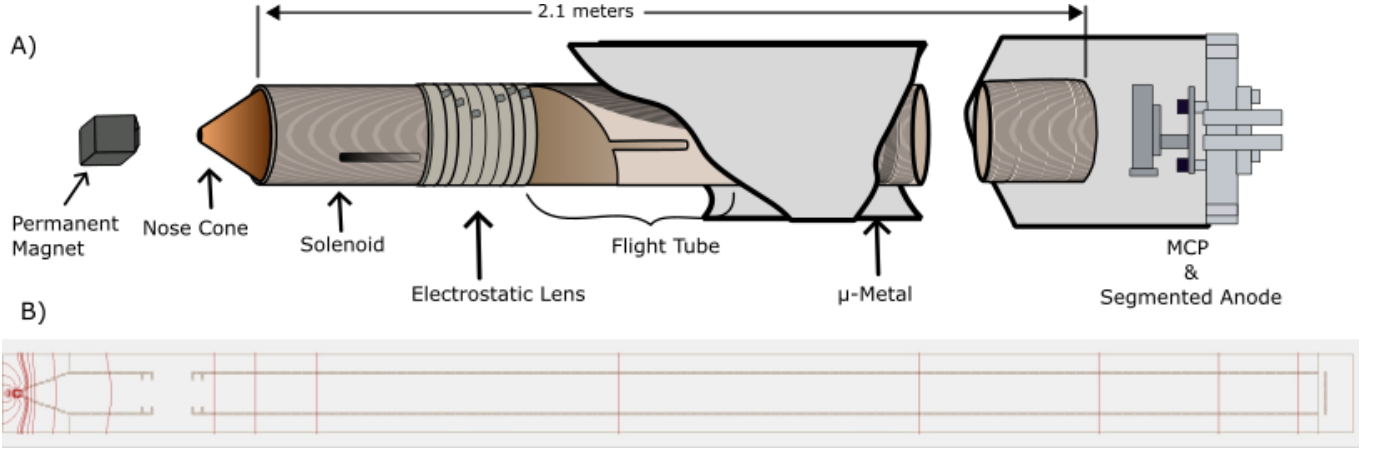


FIG. 1. **A** Schematic of the MBES. Not to scale; the length of the flight tube has been truncated in this depiction. **B** To-scale cross-section of MBES taken from the graphical representation in the SIMION software package. Contour lines show regions of equivalent magnetic field strength.

this behavior persists for all retardation voltages.

We experimentally investigate the performance of the segmented anode detector in panels **D** and **E** of Fig. 2, which show the Auger-Meitner electron spectrum of neon ionized by 1060 eV x-rays. The plot shows the measured electron distributions for the same shots, measured by the inner and outer anodes. While the outer anode has a significantly higher electron count rate, which is attributed to its much larger surface area, the energy resolution is degraded compared to the spectrum measured on the inner anode. In contrast, the resolution of the Auger-Meitner spectrum measured by the inner anode is improved but has a reduced overall count rate. We note that the performance of the segmented anode strongly depends on the alignment of the spectrometer. We achieve good alignment by maximizing the electron yield on the inner anode, by translating the permanent magnet using the motorized three-axis stage on which it is mounted.

B. Energy Calibration

We calibrate the MBES by the numerical calculation of electron trajectories using SIMION. We simulate the trajectories for electrons emitted over an isotropic distribution of emission angles, and fit the known initial kinetic energy to the simulated time of flight for different retardation voltages. To account for potential deviations from the standard $KE \propto 1/(t-t_0)^2$ behavior of a regular time-of-flight spectrometer, and an additional dependence of the calibration on the retardation voltage, we fit for a mapping from time-of-flight to kinetic energy over retardation which takes the form:

$$KE(t) = \sum_{i=0}^5 p_n \left(\frac{1}{(t-t_0)^2} \right)^n, \quad (1)$$

where $t - t_0$ is the time-of-flight of the electron referenced to its birth time t_0 and p_n is a function of retardation voltage V_R :

$$p_n = \sum_{i=0}^6 q_i^{(n)} (V_R)^i. \quad (2)$$

The dominant contribution to the fit comes from $q_1^{(0)}$, which indicates the behavior of the MBES is close to an ideal time-of-flight spectrometer where $KE \propto 1/(t-t_0)^2$, and that the mapping from time-of-flight to kinetic energy over retardation is largely independent of the value of the retardation voltage. The energy calibration agrees extremely well with our measurements, validating the accuracy of our numerical calculations for modeling the MBES.

C. Collection Efficiency

The collection efficiency of a MBES strongly depends on the kinetic energy of the electrons, the strength of the magnetic fields, and the retardation voltage applied to the electrostatic lens. Fig. 3 shows how the magnetic field strength of the solenoid influences the electron counts measured on the inner and outer anodes. This measurement was performed using nitrogen *KLL* Auger-Meitner and valence-shell photoemission from nitrous oxide (N_2O) at a photon energy of 510 eV. A retardation potential of 300 V was applied to the electrostatic lens. The magnetic field strength was controlled by scanning the current applied to the solenoid coil. As the magnetic field strength of the solenoid (applied current) is increased, we observe an approximately linear increase in the detected electron counts on the outer anode (red curve in Fig. 3), which reaches a maximum at ~ 1 A. At this field strength, the cyclotron radius of the highest energy electrons emitted perpendicular to the spectrometer axis is small enough that almost all of the emitted electrons are directed onto the detector. As the current is further increased the electron trajectories are squeezed

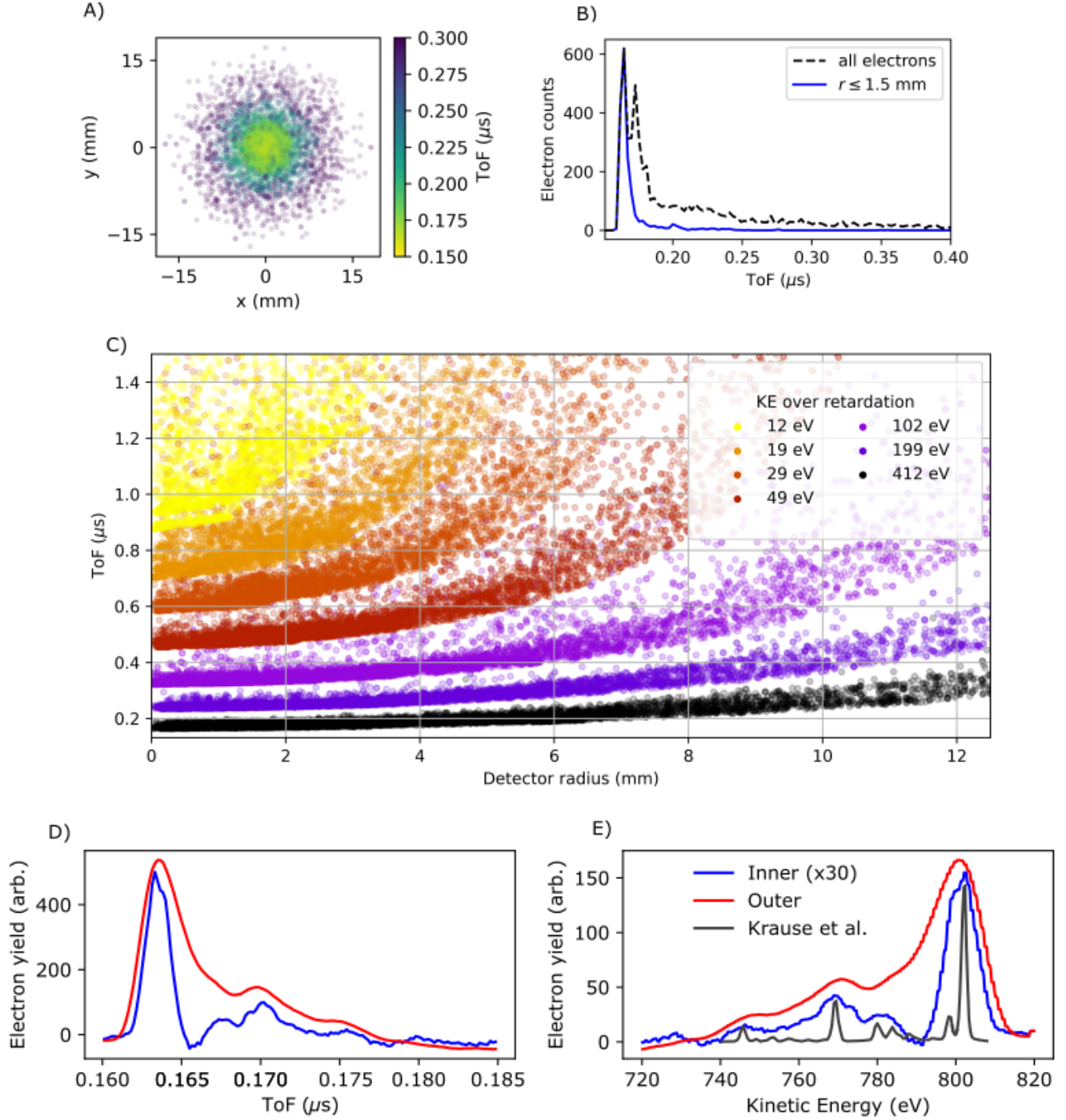


FIG. 2. Motivation and performance of the segmented anode detector. **A** Simulated spatial distribution at the detector plane of 10,000 electrons. The electrons' time-of-flight (ToF) is encoded in the color of the point. The initial kinetic energy of the electrons is ~ 812 eV and the retardation voltage is 400 V. **B** Time-of-flight spectrum for the electrons shown in panel A. The blue curve shows the ToF spectrum discriminating on electrons landing within 1.5 of the center of the detector. **C** Dependence of ToF on radius at which electrons impinge on the detector for multiple kinetic energies for a retardation of 100 V. **D** Experimental ToF spectrum for neon *KLL* Auger-Meitner electrons produced following ionization by ~ 1.35 keV x-rays, recorded with a retardation voltage of 400 V. The red curve is for electrons detected on the outer anode and the blue curve is for electrons detected on the inner anode. The signal for the inner anode has been scaled by a factor of 30. **E** Kinetic energy representation of spectra in panel D, compared to the spectrum produced by ~ 1.5 keV photons obtained using an electrostatic analyzer [33].

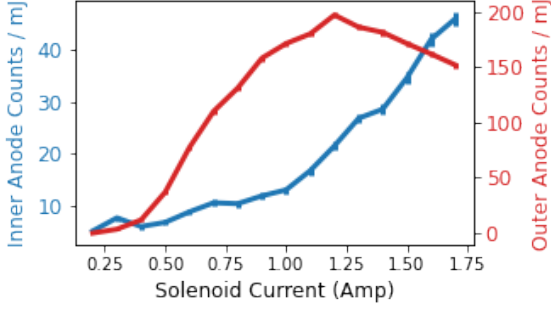


FIG. 3. Yield of nitrogen *KLL* Auger-Meitner electrons from N_2O measured on the inner and outer anodes, as a function of applied solenoid current.

closer to the center of the flight tube and more electrons impinge on the inner anode, resulting in a corresponding decrease of the electron count rate on the outer anode.

We also studied the effect of the voltage applied to the retardation lens on the MBES collection efficiency. SIMION simulations show that the collection efficiency is almost independent of electron kinetic energy when no retardation field is applied to the electrostatic lens. Once a retarding field is applied, the collection efficiency vs. kinetic energy over retardation (i.e. the final kinetic energy of the electron through the flight tube) has a weak dependence on the applied retardation voltage. This behavior is illustrated in Fig. 4 A.

We validate the performance of our SIMION model using the measured yield of ~ 100 eV nitrogen *K*-shell photoelectrons ionized from N_2O by 510 eV x-rays. The black points in Fig. 4 B show the electron yield as a function of kinetic energy over retardation. This data was collected by scanning the applied retardation voltage while keeping the x-ray photon energy fixed at 510 eV. The colored lines show the simulated detection efficiency for different retardation voltages selected from panel A. In both experiment and simulation, we observe a steep decrease in collection efficiency as the retardation voltage approaches the initial kinetic energy of the electron. Panel C shows the region of panel A corresponding to retardation voltages below 50 V. At lower retardation voltages and kinetic energies, the detection efficiency depends more strongly on the retardation voltage.

D. Electron-electron covariance

To demonstrate an advantage of a high collection efficiency electron spectrometer such as our MBES, we performed an electron/electron covariance measurement on an N_2O target ionized by 790 eV x-rays. Ionization of the nitrogen *K*-shell produced photoelectrons with a kinetic energy of ~ 390 eV. The core-ionized molecule decayed *via* Auger-Meitner emission, leading to the emission of a second electron with a kinetic energy of ~ 350 eV. A schematic of this decay process is shown in Fig. 5A. We measure the kinetic energy spectrum of the resultant electrons with our MBES, using a retardation

voltage of 250 V applied to the electrostatic lens. For this measurement, we made use of the electrons detected on the outer anode to improve the effective collection efficiency of the MBES. We calculated the autocovariance of the electron kinetic energy spectrum across $\sim 40,000$ XFEL shots [23]:

$$\text{Cov}[\vec{Y}, \vec{X}] = \langle \vec{Y} \cdot \vec{X} \rangle - \langle \vec{Y} \rangle \langle \vec{X} \rangle, \quad (3)$$

where $\vec{X}$ is the electron kinetic energy spectrum, $\vec{Y} = \vec{X}^T$, and operator $\langle \cdot \rangle$ indicates an average across the measured laser shots. Fig. 5 B shows a small region of the resultant covariance map. This map is dominated by strong covariance islands between electrons of kinetic energy $\sim 330 - 400$ and ~ 265 eV, which lie directly below the horizontal black line at 280 eV. Electrons with kinetic energy $\sim 380 - 400$ eV correspond to direct ionization from the $\text{N}1s$ shell, while electrons with energy $\sim 340 - 360$ eV are produced by nitrogen Auger-Meitner emission. The electrons at ~ 265 eV are produced by ionization from the oxygen *K*-shell.

In XFEL measurements, the shot-to-shot fluctuations of the spectral profile and pulse energy of the incoming x-ray pulse can produce spurious covariance islands which do not reflect the correlated emission of two photoproducts from the same ionization pathway. To remove these uninteresting correlations, here we calculate the multivariate partial covariance:

$$\text{pCov}[\vec{Y}, \vec{X}; \vec{I}] = \text{Cov}[\vec{Y}, \vec{X}] - \text{Cov}[\vec{Y}, \vec{I}] \left(\text{Cov}[\vec{I}^T, \vec{I}] \right)^{-1} \text{Cov}[\vec{I}, \vec{X}], \quad (4)$$

where $\vec{I}$ is the single-shot x-ray spectrum and $\left(\text{Cov}[\vec{I}^T, \vec{I}] \right)^{-1}$ is the inverse of the autocorrelation of the spectrum. This partial covariance map is shown in Fig. 5 B. In this map we observe that the spurious correlation between the electrons at $\sim 330 - 400$ and ~ 265 eV has been suppressed. We also observe a strong positive correlation away from the diagonal of the map, indicating that the emission of electrons with ~ 390 eV of kinetic energy is correlated with the emission of the 360 eV Auger-Meitner electrons as illustrated in panel A. This is a direct experimental observation of the photoelectron/Auger-Meitner electron emission process following *K*-shell ionization of N_2O . The kinetic energy structure of the Auger-Meitner emission results from the population of different final states in the N_2O dication. We note that the nitrogen photoelectron features have a dual peak structure. This is the result of the average spectral intensity of the incoming x-ray spectrum, which has a double-peak structure as shown in an inset in each panel.

E. Spatial Sensitivity of MBES

In contrast to open area spectrometers (such as traditional VMI [34] or COLTRIMS [35]) time-of-flight spectrometers collect electrons from a localized region. In a magnetic bottle spectrometer the volume of the collection region is small, due to the strong spatial localization of the magnetic field. This spatial selectivity offers the opportunity to perform photoionization measurements which are highly selective to different positions along the focus of the ionizing radiation.

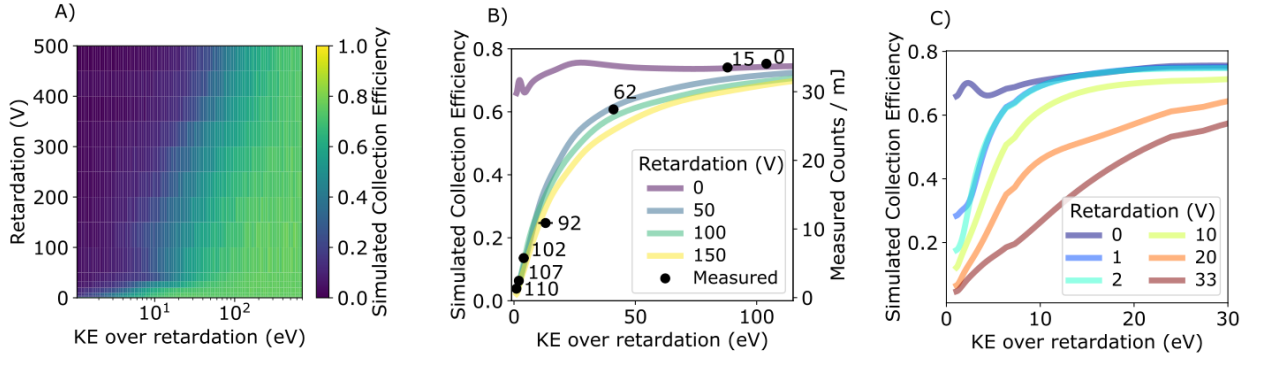


FIG. 4. **A** Simulated values of the detection efficiency as a function of retardation voltage and kinetic energy over retardation. **B** Comparison of simulated detection efficiencies from panel **A** with experimentally measured yield of ~ 100 eV photoelectrons measured at different retardation voltages (black points). **C** Simulated electron transmission from panel **A** for lower retardation voltages and electron kinetic energies.

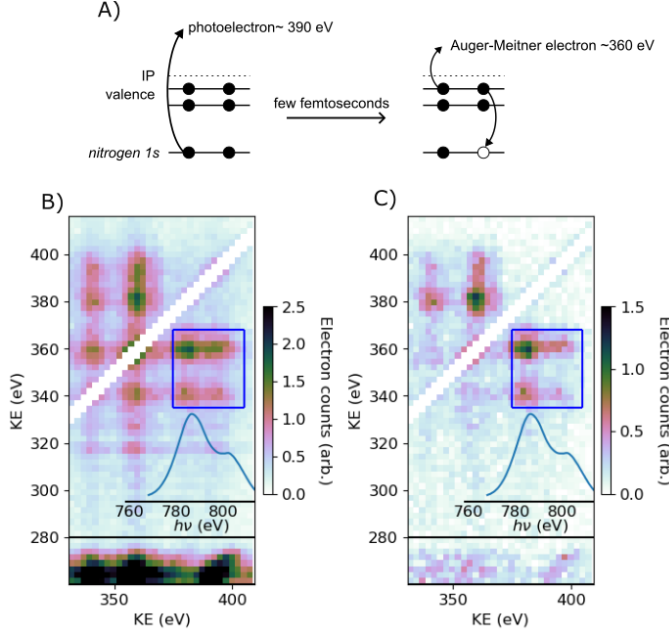


FIG. 5. **A** Schematic of Auger-Meitner decay following nitrogen K -shell photoionization of N_2O by ~ 790 eV x-rays. **B** Region of covariance map (Eqn. 3) of the electron kinetic spectrum following 790 eV ionization of N_2O . **C** Partial covariance map (Eqn. 4) demonstrating suppression of spurious correlations in panel **B**. This reveals correlation between photoelectrons from ionization of the nitrogen K -shell (~ 380 - 400 eV) and Auger-Meitner emission (~ 340 - 360 eV), highlighted with the blue rectangle. The inset shows the average spectral profile of the incoming x-ray pulse, which produces the bimodal structure of the nitrogen K -shell photoelectron spectrum.

The collection efficiency of the MBES is sensitive to the alignment between the permanent magnet, the flight tube and the electron source. We can optimize the spectrometer alignment using the three-axis manipulator on which the magnet is mounted. We plot the dependence of the electron yield on the magnet position in Fig. 6 **B**, which is sensitive to the spatial

selectivity of the MBES. This measurement was performed using electrons with ~ 100 eV kinetic energy produced by nitrogen K -shell ionization of N_2O by ~ 510 eV x-rays. No retardation potential was applied to the lens. We observe a nearly equal dependence on collection efficiency for magnet motion along the axes perpendicular to the flight tube (y and z -axes), with a collection length of ~ 1 mm. The reduced sensitivity along the axis of the spectrometer (x -axis) is expected. Moving the magnet in this direction can affect the collection efficiency of electrons depending on their initial direction of emission [15]. The measurement shown in Fig. 6 is sensitive to the spatial selectivity of the MBES, but does not allow for its direct characterization. This is because we were unable to change the alignment between the flight tube and the electron source. Moreover, at the beam parameters available for the experiment the electron signal was produced by linear x-ray interactions. As a result, our effective electron source was highly extended along the direction of beam propagation. Nonetheless, we are able to investigate the spatial selectivity of the MBES in simulation. For similar parameters as the measurement shown in Fig. 6 **B** (103 eV KE electrons, 0 V retardation), we simulate the spatial selectivity of the MBES by displacing a point source of electrons, emitted in a uniform distribution across the unit sphere, in a MBES where the magnet and flight tube are fully aligned. The direction of the source point displacement is perpendicular to the flight tube axis, which corresponds to any direction in the yz plane illustrated in panel **A**. The simulated dependence of detection efficiency on the source point position is shown in panel **C**. We observe that in a well-aligned MBES, it is possible to strongly limit the collected electrons to a source with a spatial extent around $100 \mu\text{m}$.

F. Energy Resolution

To investigate the energy resolution of the MBES and characterize the effect of the retardation lens, we performed a systematic scan of the retardation voltage. A higher retarda-

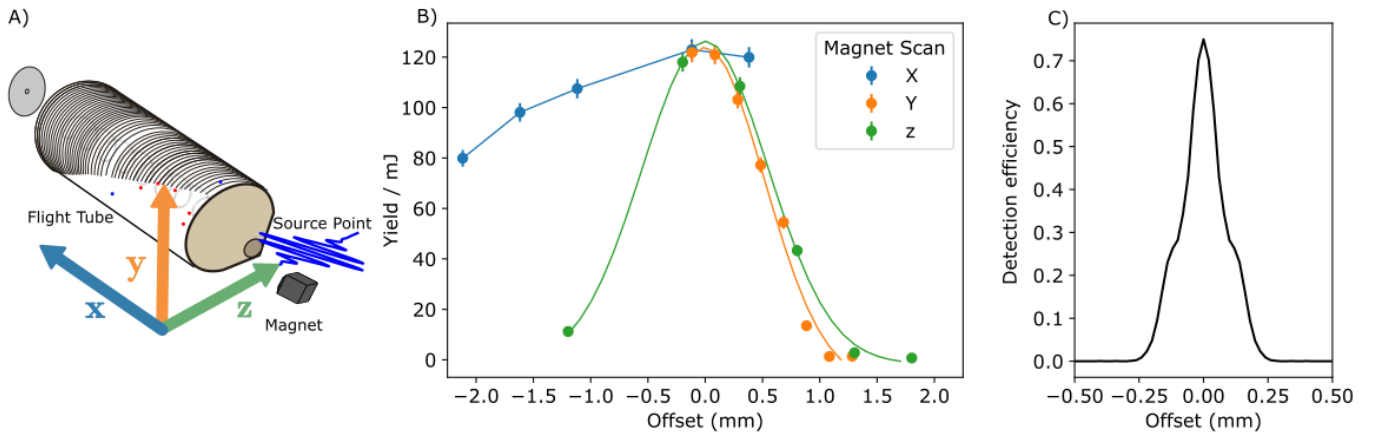


FIG. 6. **A** Schematic illustrating the coordinate definitions: x : time-of-flight axis of the magnetic bottle and x-ray polarization direction, y : axis of the diffusive gas jet; z : direction of x-ray propagation. **B** Electron yield from N_2O ionized by 516 eV x-rays as a function of magnet alignment according to coordinate definitions in panel A. **C** Simulated collection efficiency of the MBES for a point source of electrons displaced from the interaction point by the yz plane.

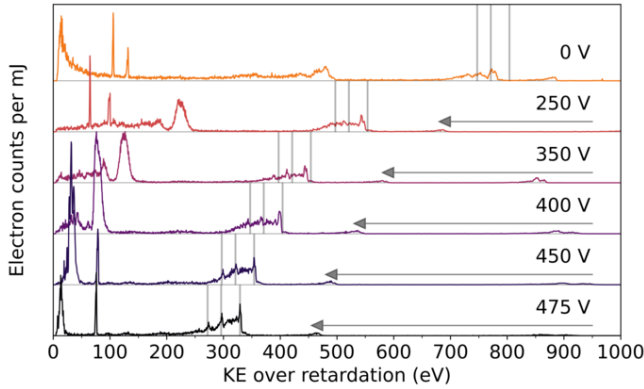
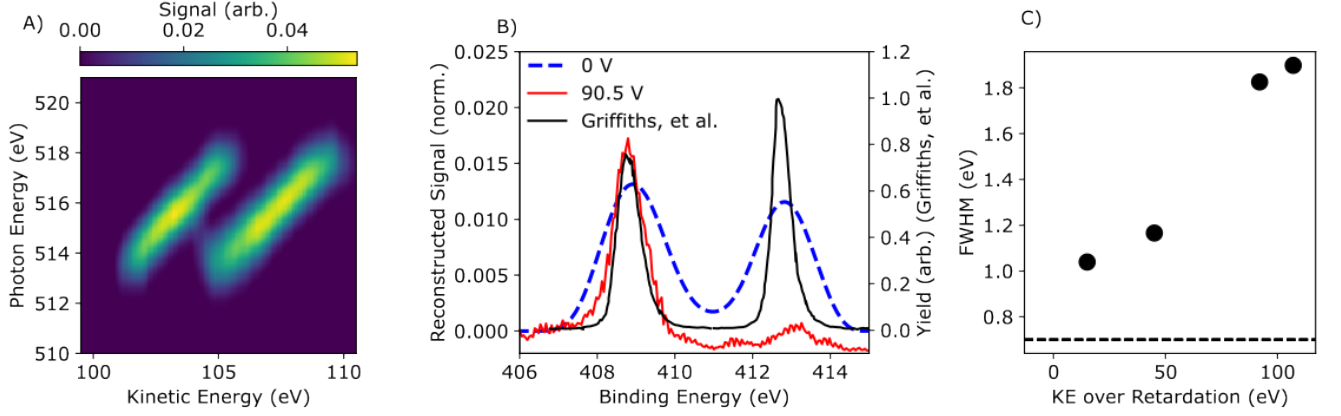


FIG. 7. Photoelectron kinetic energy spectrum of neon recorded at a photon energy of 1.35 keV. The three primary peaks of the Ne KLL Auger-Meitner emission spectrum become increasingly better resolved as the voltage applied to the electrostatic retardation lens is increased. The three dashed lines correspond to previously measured values of these features [33].

tion voltage is expected to produce higher energy resolution, because the energy resolution of an MBES $\delta E/E$ is approximately linearly proportional to $\Delta T/T$ [13]. Fig. 7 shows the measured photoemission kinetic energy spectrum of neon gas ionized by ~ 1.35 keV x-rays. We record this spectrum at six different retardation voltages, as indicated on the figure. The neon KLL Auger-Meitner emission has three dominant features separated by ~ 30 eV, corresponding to different final states of the neon dication [33]. The expected energetic position of these three features is indicated by the vertical dotted lines. We observe that increasing the retardation voltage improves the energy resolution of the spectrometer: at higher retardation voltages the three primary KLL emission lines appear more clearly separated.

To quantify the resolving power of the MBES, we measured the widths of the photoionization features produced by K -shell ionization of N_2O as a function of retardation voltage. This measurement was performed using x-rays with a central photon energy of ~ 516 eV. The target molecule was chosen because the nitrogen K -shell photoemission spectrum of N_2O is well-studied and consists of two features corresponding to ionization of the central and terminal nitrogen sites at 412.5 eV and 408.5 eV, respectively [36]. The SASE FEL has a broad (~ 5 eV) spectral bandwidth and inherent shot-to-shot fluctuations in the spectral profile, which can significantly degrade spectroscopic resolution. To mitigate the effect of the SASE bandwidth and spectral jitter, and isolate the resolution of the MBES, we employed spectral domain ghost imaging [28, 37], as described in the appendix.

An example of the two-dimensional map of photoelectron kinetic energy *vs.* incoming photon energy is presented in Fig. III F A. We extract the kinetic energy spectrum from the two-dimensional map by averaging across all photon energies after accounting for the energy dispersion of the photoelectron. The width of the measured photoelectron feature for different retardation values is shown in Fig. III F B and can be seen to decrease with increasing retardation. The MBES detection efficiency at very low values of kinetic energy over retardation is highly suppressed, as shown in Fig. 4. This effect results in a significant decrease in yield for the lower energy photoelectrons at a retardation of 90.5 V. We quantify the resolution by fitting a gaussian curve to the photoline of the terminal nitrogen site at 107 eV. The dependence of this width on retardation is shown in Fig. III F C. The results show that when there is no retardation voltage applied, it is still possible to discern the 4 eV separation between the central and terminal lines thanks to the long flight tube. Nonetheless by increasing the retardation voltage, the kinetic energy resolution can be significantly increased.



B Binding energy spectrum for N(1s) photoionization of N₂O obtained from dispersion plot in panel A. The measured peak width decreases with increasing retardation voltage. Black line shows previous high-resolution measurements made with a synchrotron source from [36]. The change in relative intensities at larger retardation voltages is a result of the MBES transmission function, see Fig. 4. **C** Widths corresponding to gaussian fits of the terminal photoline centered at 408.5 eV binding energy. The dashed black line at 0.70 eV corresponds to the measured width from reference [36].

B Binding energy spectrum for N(1s) photoionization of N₂O obtained from dispersion plot in panel A. The measured peak width decreases with increasing retardation voltage. Black line shows previous high-resolution measurements made with a synchrotron source from [36]. The change in relative intensities at larger retardation voltages is a result of the MBES transmission function, see Fig. 4. **C** Widths corresponding to gaussian fits of the terminal photoline centered at 408.5 eV binding energy. The dashed black line at 0.70 eV corresponds to the measured width from reference [36].

IV. ENERGY-DEPENDENT MODULATION IN ELECTRON TRANSMISSION EFFICIENCY

Finally, we discuss an artifact that is common to magnetic bottle electron spectrometers, namely a strongly energy-dependent modulation of the electron transmission function which is often amplified when a retarding field is applied to the electrostatic lens. This artifact is a result of the betatron oscillations of the electrons as they travel through the magnetic-field of the flight tube and propagate toward the detector [38]. The cyclotron radius of these oscillations,

$$r_C = \frac{\sqrt{2m_e KE}}{e_0 |\vec{B}|} \sin \theta_f, \quad (5)$$

depends on the electron kinetic energy KE , the strength of the magnetic field $\vec{B}$, and the angle of the electron velocity relative to the flight tube axis, θ_f . The effect of this cyclotron motion is to induce a periodic modulation in the transverse distribution of electron trajectories as they move along the flight tube. The spatial period of the modulation, i.e. the distance between points where the electron spread is maximal, depends on the kinetic energy of the electron [38]:

$$l_o(KE) = 2\pi \frac{\sqrt{2m_e KE}}{e_0 |\vec{B}|} \cos \theta_f. \quad (6)$$

The size of the electron spatial distribution at the detector is therefore a function of the velocity of the electrons. If the

flight tube is an integer multiple of l_o , then the spatial extent of the electrons is quite small at the detector plane. In the other limiting case, if the flight tube length is a half-integer multiple of l_o and the spatial extent of the electron distribution is maximal at the detector plane. The energy-dependent oscillations have consequences for the operation of a MBES: electrons arriving at the detector plane with radial displacement larger than the detector can miss the detector and fail to be detected. Thus, the electron detection efficiency of the MBES is periodically modulated with electron time-of-flight. In our spectrometer, there may be an additional decrease in transmission efficiency due to electrons impinging on the plates of the electrostatic retardation lens. This additional effect should be particularly pronounced at high retardation voltages, due to fringe fields from the electrostatic lens that act perpendicular to the time-of-flight axis.

This oscillatory behavior of the electron trajectories is illustrated in the simulations shown in Fig. 9. We plot ten trajectories of electrons emitted in arbitrary directions uniformly sampled on a sphere, with ~ 300 eV initial kinetic energy. The dependence of the cyclotron radius on the direction of the electron velocity described in Eq. 5 manifests as the dependence of the trajectory on the initial emission angle, as shown in panel C. This effect is often colloquially referred to as ‘sausaging’, because the three-dimensional shape of the electron trajectories through the flight tube is reminiscent of the shape of a link of sausages.

This oscillatory collection efficiency is observed in ex-

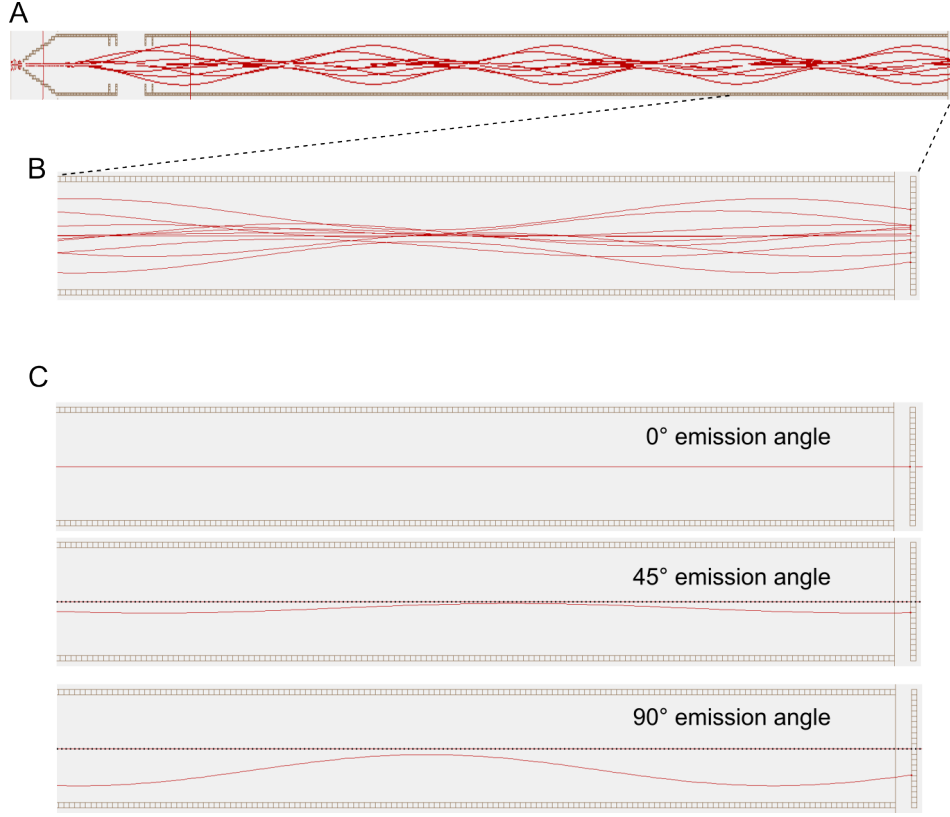


FIG. 9. **A** SIMION simulation of trajectories of ~ 300 eV electrons with different initial emission directions through the MBES. The retardation voltage is 0 V and the solenoid current has been reduced from the standard operation parameters to amplify the radius of the cyclotron oscillation. **B** Zoom-in of the trajectories at the end of the flight tube, close to the electron detector. **C** Dependence of electron trajectories through the flight tube on the angle of direction of initial emission, relative to the flight tube axis. The dotted black line shows the central axis of flight tube.

periment in the measured electron time-of-flight spectra of x-ray (520 eV) ionization of N_2O molecules, shown in Fig. 10 **A**. The strong periodic modulation of electron detection efficiency with the electron time-of-flight is apparent in the spectrum recorded on the inner anode of the detector. According to Eqn. 6, the modulation frequency should increase with increasing magnetic field, and thus increasing solenoid current. This effect can be seen in Fig. 10 **B** and **C**, where the Fourier transform of the electron time-of-flight spectra recorded on the outer (**B**) and inner (**C**) sections of the detector is shown as a function of the current applied to the solenoid coil. There is a dominant Fourier component, indicated by the white dashed-line, whose frequency increases linearly with solenoid current in accordance with the well-known dependence of cyclotron frequency on magnetic field strength. Below ~ 1.1 A, the modulation is particularly pronounced on the outer section of the detector (outer anode), while above this value the effect dominates the inner anode. This is a result of the geometry of the two detectors: as we increase the solenoid current, the electron trajectories flatten to the central axis of the flight tube and the modulation amplitude grows stronger on the inner anode and less prominent on the outer.

One solution to the periodic modulation in electron detection efficiency is to increase the solenoid current to reduce

the cyclotron radius such that all electrons fall on the detector. However, increasing the solenoid current to the required value may be technically challenging, and also results in a decrease of electron energy resolution [13]. Instead we developed an analytical method to remove this artifact in data post-processing [39]. We demonstrate this routine using the electron spectrum recorded by our MBES following the ionization of gas-phase para-aminophenol at ~ 252 eV. The time-of-flight spectrum was recorded with a retardation of 190 V and is shown in Fig. 11 **A** before (dashed red) and after (dashed blue) removal of this artifact.

To remove the artifact, we treat the measured electron spectrum $D(t)$ as a product of the true electron spectrum $S(t)$ and the transmission function that encodes the periodic features, which we approximate as $T_s(t) = 1 - a \cos(\omega_s t)$, where ω_s is the period of oscillation in the transmission function. The measured data can then be written as

$$D(t) = S(t)T_s(t) = S(t)(1 - a \cos(\omega_s t)). \quad (7)$$

Filtering out the modulation frequency (ω_s) from this transmission function with a Fourier filter will result in data loss because the Fourier transform of $D(t)$ is given by the convo-

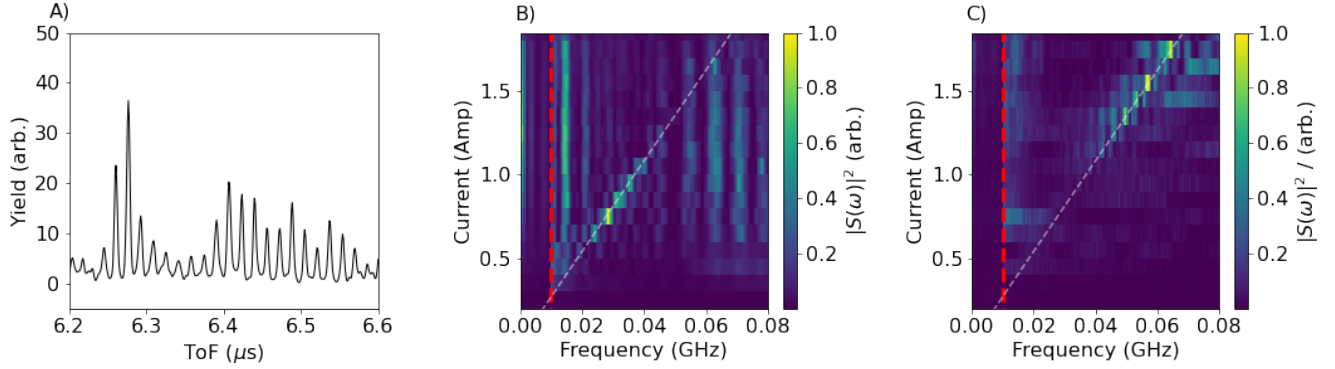


FIG. 10. **A** Time-of-flight (ToF) spectrum for photoelectrons produced by ionization of N_2O by 520 eV x-rays, measured on the inner anode at a solenoid current of 2 A, showing a strong periodic modulation in detection efficiency. **B** Fourier transform of the ToF spectra as a function of applied solenoid current for the outer anode. **C** Fourier transform of the ToF spectra as a function of applied solenoid current for the inner anode. For frequency values greater than 0.01 GHz, the color scales in panels **B** and **C** have been multiplied by 50 and 25, respectively.

lution rather than the sum,

$$\tilde{D}(\omega) = (\tilde{S} * \tilde{T}_s)(\omega) \propto 2\tilde{S}(\omega) - a(\tilde{S}(\omega - \omega_s) + \tilde{S}(\omega + \omega_s)). \quad (8)$$

Attempts to filter out the shifted copies of $\tilde{S}$ are likely to modify the extracted spectrum.

To avoid this problem, we first take the logarithm of the spectrum, which separates the ground truth spectrum and transmission function into a sum, which can be more easily separated by Fourier decomposition:

$$\ln(D(t)) = \ln(S(t)T_s(t)) = \ln(S(t)) + \ln(1 - a\cos(\omega t)). \quad (9)$$

The final term can be written as a Fourier series as,

$$\begin{aligned} \mathcal{F}(\ln(D))(\omega) &= \mathcal{F}(\ln(S))(\omega) - \ln\left(1 + \frac{a^2}{4}\right) \delta(\omega) \\ &\quad + a(\delta(\omega - \omega_s) + \delta(\omega + \omega_s)) \\ &\quad + \frac{a^2}{4}(\delta(\omega - 2\omega_s) + \delta(\omega + 2\omega_s)) + \mathcal{O}(a^3). \end{aligned} \quad (10)$$

The broadening at the harmonic 0.045rad/ns due to the convolution in Eq. 8 is replaced by a narrowed peak after applying the logarithm, as shown in Fig. 11 **B**. To recover the signal $S(t)$, we filter out the harmonics of ω_s from the log-scaled spectra using Butterworth filters to generate the frequency-domain filtered data $\mathcal{F}(\ln(D))(\omega)$. To recover the filtered data in real space $D_f(t)$, we apply an inverse Fourier transform and then exponentiate. This method of examining the Fourier transform of the logarithm has been used to study situations where the Fourier transform contains periodic peaks, because it maps the convolution of two functions onto their sums [40].

We also implemented the log-space Fourier filter algorithm on a two-dimensional measurement of the resonant oxygen Auger-Meitner emission from para-aminophenol. The X-ray photon energy was scanned over the oxygen K -edge region

from ~ 505 to ~ 550 eV, and the high-energy electron emission spectrum was recorded with 400 V applied to the electrostatic lens. The resonant Auger-Meitner map (incoming x-ray photon energy vs. outgoing photoelectron energy) is shown in Fig. 12. The photoelectrons produced by x-ray ionization of the valence shell show a clear linear dispersion, and the resonant Auger-Meitner emission after promotion of an electron from the oxygen $1s$ to the $2p\pi^*$ orbital is clear at ~ 532 eV. Above the oxygen $1s$ ionization potential, the electron emission converges to the normal KLL Auger-Meitner emission.

In the left panel, the periodic modulation is clearly seen and is most apparent in the resonant and normal Auger-Meitner emission at higher photon energies. We note that this modulation does not disperse with photon energy because it is a function of electron time-of-flight only. Removal of this periodic modulation has been performed by an enhanced application of the algorithm described above. To eliminate the possibility of distorting the two-dimensional map, a single transmission function $T(t)$ was developed and then applied uniformly to each photon energy bin as

$$D_f(t, h\nu) = D(t, h\nu) / T(t) \quad (11)$$

where $D_f(t, h\nu)$ denotes the two-dimensional filtered data. To compute the transmission function, the raw data is summed over photon energy and the 1D curve is filtered. By dividing the unfiltered and filtered data, a robust transmission function can be developed as

$$T(t) = D_{all}(t) / D_{all,f}(t) \quad (12)$$

This transmission function is more robust compared to treating each photon energy bin separately, because the filter is nonlinear. By increasing the statistics when calculating the transmission function, we can more effectively filter the periodic transmission function.

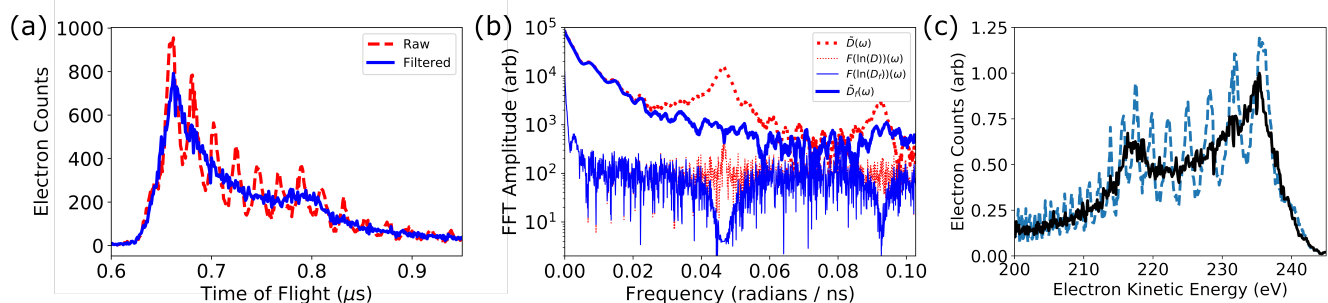


FIG. 11. Demonstration of the filtering algorithm to remove structure caused by betatron motion of electrons in the magnetic bottle for the x-ray valence ionization spectrum of para-aminophenol. **A** Time-of-flight representation with the raw spectrum showing the artefact before (dashed red) and after (blue) applying the filtering algorithm. **B** FFT power spectrum at different points in the filtering algorithm. Red lines show the spectrum of the raw data before (tick dotted red line) and after (thin dotted red line) taking the logarithm, i.e. $D(\omega)$ and $\mathcal{F}(\ln(D))(\omega)$. Blue lines show the spectrum of the log-filtered data before (thick blue line) and after (thin blue line) exponentiating, i.e. $F(\ln(D_f))(\omega)$ and $\tilde{D}_f(\omega)$. **C** Data in the electron kinetic energy representation before (blue dashed line) and after (black line) the filtering algorithm.

V. CONCLUSION

In this paper, we have presented the design and performance of a MBES for x-ray photoelectron spectroscopy. Our spectrometer is installed at the TMO endstation of the Linac Coherent Light Source and is available to users of the facility. It is equipped with an einzel-stack retardation lenses and a segmented anode, which enables high kinetic-energy resolution ($\delta E/E \sim 1\%$) measurements of high energy (several hundred eV) photoelectrons. The segmented anode also enables the simultaneous collection of data in two different modes: high collection efficiency, using electrons detected on both anodes, and high resolution, using only electrons detected on the inner anode. We achieve high energy x-ray photoelectron spectroscopy measurements when coupled to a noisy x-ray free-electron laser by employing spectral domain ghost imaging, and we achieve covariance measurements of correlated photoelectron/Auger-Meitner electron emission from N_2O . We present a robust analysis procedure to correct for the well-known periodic modulation in detection efficiency due to cyclotron motion of the electron in the MBES flight tube. Upgrades to the instrument will include the integration of an ion time-of-flight spectrometer for concurrent ion/electron spectroscopy. Our spectrometer can currently be used for a variety of user experiments, and will be capable of operating in the MHz regime with the the upgraded high-repetition-rate LCLS-II source.

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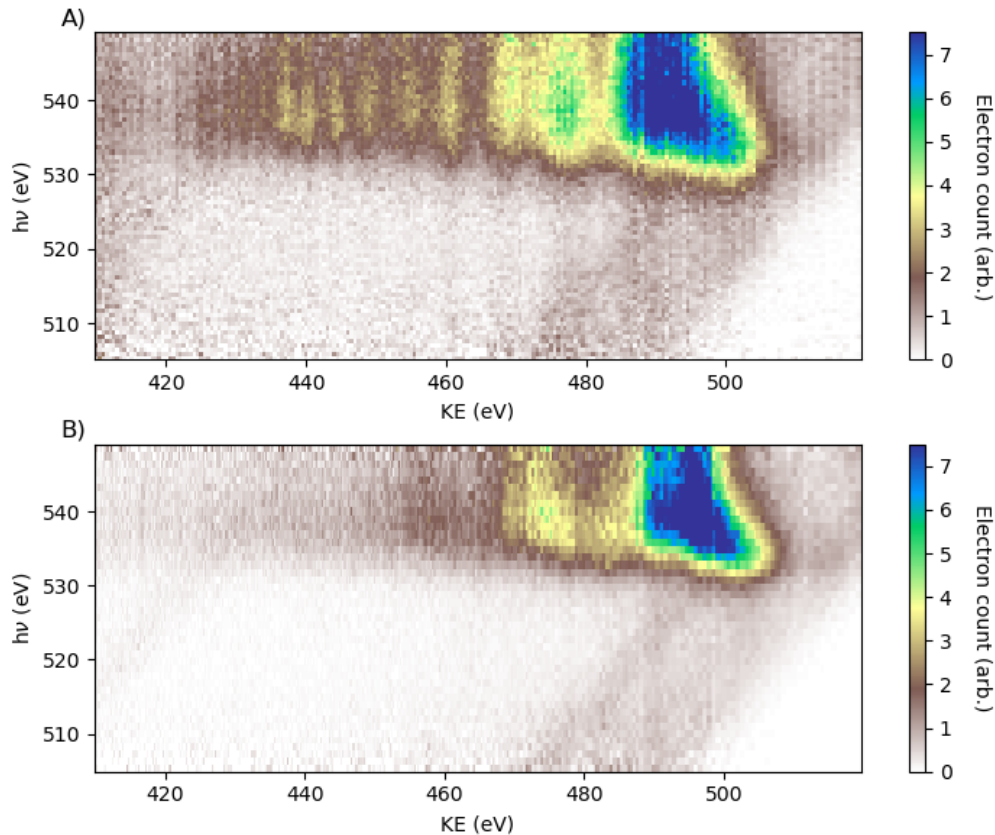


FIG. 12. Resonant oxygen Auger-Meitner spectra of para-aminophenol before (A) and after (B) the filtering algorithm to remove the periodic modulation in detection efficiency. The x -axis shows the electron kinetic energy spectrum measured with a retardation of ~ 400 eV and the y -axis shows the x-ray central photon energy. Between x-ray photon energies of 530–535 eV we observe resonant Auger-Meitner emission following resonant oxygen $1s \rightarrow$ valence excitation. At photon energies above 535 eV, the spectrum converges to regular oxygen KLL Auger-Meitner emission. We also observe dispersive lines due to x-ray valence ionization.

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VII. APPENDIX

A. Spectral Domain Ghost Imaging

Spectral domain ghost imaging exploits the correlation between electron and x-ray photon spectra on a single-shot basis to extract the spectral response of the sample under investigation [27–29, 41]. In the single photon regime, the correlation of the photoelectron spectra with the photon flux of the incident x-ray pulse, can be represented as a system of linear equations $Ax = b$. A and b are matrices whose columns index the spectral bins of the photon and electron energy spectra respectively, and whose rows correspond to different shots. The unknown partial ionization cross section is encoded in the x matrix. Due to the inherent measurement noise in A and b , determining x via least-square optimization is typically a numerically unstable operation. Therefore, we solve for x by minimizing the following cost function, which includes regularization parameters which enforce known qualities of the solution x :

$$\|Ax - b\|_2^2 + \lambda_1 \|x\|_1 + \lambda_2 \|Lx\|_2^2 + \text{Ind}_+(x) \quad (13)$$

Here, the λ are hyperparameters that weight the different regularization terms. For the measurements presented in this work, the first term imposes sparsity defined by the L_1 -norm λ_1 and the second term imposes smoothness λ_2 , defined by the laplacian operator. The last term imposes non-negativity in x . We employed a quadratic programming optimization [42, 43] to minimize equation 13 and obtain the optimal value of x . We choose the values of the hyperparameters by selecting appropriate values along the L-hypersurface [44, 45]. For all measurements, the spectral response x was robust to the values of the hyperparameters over several orders of magnitude.

3.5 Time-domain ghost imaging for pump/probe experiments at high repetition rate

This section includes work discussing the developments of time-domain ghost imaging (TDGI) for correlating fast and slow acquisition detectors for improved temporal resolution in pump-probe experiments. At the time of writing this thesis, this manuscript is in review.

This manuscript discusses the mathematical framework of this TDGI method and its efficacy using a real time-resolved X-ray absorption measurement.

I helped with the experimental setup for this beamtime, along with the rest of the TMO team. I analyzed the data online and offline, wrote the draft, and prepared the manuscript with feedback from all coauthors.

The analysis for this experiment was done in close collaboration with coauthors Martin Graßl and principle investigator Thomas Wolf.

Time-Domain Ghost Imaging for Pump/Probe Experiments at High Repetition Rate

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(Dated: 11 July 2024)

We employ time-domain ghost imaging to improve the temporal resolution in pump-probe experiments conducted with high-repetition rate light sources such as free-electron lasers (FELs). Many detectors have a data acquisition rate significantly slower than the repetition rate of these state-of-the-art light sources, necessitating averaging a signal over several laser shots. If the intended pump-probe delay exhibits shot-to-shot instability, or jitter, the temporal resolution is degraded. For measurements using FELs driven by self-amplified spontaneous emission (SASE), the degree of jitter can be several orders of magnitude larger than the dynamics under investigation. In this study, we show that by correlating an observable averaged across multiple shots with another measurement that characterizes the laser-FEL pump-probe jitter on a single-shot basis, it is possible to recover the same time resolution as a single-shot measurement. We demonstrate this technique using a time-resolved x-ray absorption measurement performed at the Linac Coherent Light Source (LCLS) x-ray FEL. We show that our method is robust to significant temporal jitter and long integration windows of the slow detector.

I. INTRODUCTION

The development of pump-probe spectroscopy using ultrafast laser pulses has enabled the measurement of molecular dynamics on their natural timescale. By scanning the delay between two ultrafast pulses with femtosecond-scale precision and measuring the resultant changes in an observable, it is possible to directly observe molecular motion.

Increasing the repetition rate in such experiments improves the measurement fidelity and enables more information-rich measurements by scanning additional parameters. Ultrafast laser sources with pulse repetition rates in excess of one hundred kilohertz are now readily available. This surpasses the data acquisition rate of many X-ray large-area detectors [1–3], which are therefore only able to record an observable averaged over multiple laser shots. This can be problematic if the parameters of the experiment vary from shot-to-shot, as is the case for measurements conducted with a self-amplified spontaneous emission free-electron laser (SASE-FELs). SASE-FELs offer a versatile suite of probing techniques, such as coherent scattering, soft x-ray spectroscopy, and x-ray correlation spectroscopy [4, 5]. These measurements have enabled powerful new insights into the ultrafast dynamics of gas and condensed phase systems. In the case of x-ray absorption or photoelectron spectroscopy, the spectral resolution can be limited by the large bandwidth of ultrafast x-ray pulses, as well as the shot-to-shot spectral fluctuations inherent to SASE operation. Frequency-domain ghost imaging has been developed to address this problem. In this method, the single-shot fluctuations in the SASE spectrum are correlated with the experimental observable, to achieve sub-bandwidth resolution [6–

9]. In this paper, we employ the same mathematical framework in experiments where the measurement of the observable is acquired over multiple shots, and in correlating this measurement with a single-shot jitter diagnostic, can recover the temporal resolution to that of a single-shot measurement.

In time-resolved pump-probe measurements, dynamics are initiated (or pumped) by a laser pulse and probed by the FEL pulse after a certain time delay. For many FELs, the laser pump and FEL probe pulses are not perfectly synchronized and their relative timing can vary randomly on a single-shot basis. This can be due to radio-frequency (RF) noise, thermal fluctuations, spatial drifting between the beams and additional instabilities that are inherent to the nature of SASE operation [10]. Arrival time monitors (ATMs) have been implemented to account for this timing jitter in pump/probe experiments and improve the temporal resolution [11–14]. The pump-probe delay measured by the ATM is typically used to correct for jitter, on a shot-to-shot basis, in post-processing of the data. This procedure has been suitable thus far for the <1 kHz repetition rates of the first generations of FELs.

Next generation of XFEL facilities will provide repetition rates in excess of 100 kHz. Many state-of-the-art detectors, however, have acquisition periods significantly longer than the expected spacing between consecutive shots from these FELs. Because these ‘slower’ detectors will integrate over several FEL shots, the temporal resolution of pump-probe experiments will be limited by the x-ray/laser timing stability in the integration window. In the presence of pump/probe jitter, this can be problematic. In this work, we overcome this timing-jitter limitation using the technique of time-domain ghost imaging (TDGI) [15]. Using experimental data from a time-resolved x-ray absorption measurement, we correlate the

single-shot measurement of the arrival time with an average measurement of the observable to realize the same temporal resolution achievable with a single-shot measurement of the observable. Our work builds on the proposed implementations of time-domain ghost imaging at FELs [16]. A schematic of the measurement technique is shown in figure 1. The mathematical framework we use is identical to that which we have employed in previous work on frequency-domain ghost imaging [6–8, 17, 18].

Our measurement was performed at the Time-resolved AMO endstation of the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory [19]. The sample, acetophenone, was introduced to the interaction region by an effusive needle seeded with 27 psi of helium. Ultraviolet (UV) pump pulses with a central wavelength of 268 nm were overlapped with soft X-ray pulses probe tuned to the oxygen *K*-edge spectral region. The transient absorption signal appeared at an absorption energy between 527.00 and 527.50 eV. The absorption was measured by recording the yield of resonant Auger-Meitner electrons emitted at a kinetic energy between 500–530 eV, using a 2 m long magnet bottle electron spectrometer (MBES). The arrival time between the laser and FEL pulses was measured using a single-shot cross-correlator arrival time monitor (ATM) [14]. The ATM uses a spatially-encoded interferometric scheme, with the time delay encoded from the X-ray modified reflection of an IR-beam that is sourced from the same laser as the pump-beam in the experiment. The reflection is imaged with a fast camera, and the single-shot images are integrated over the horizontal direction, revealing a one dimensional trace with a distinct edge indicative of the IR X-ray overlap. Examples of these traces are shown in 1A). The full temporal range for this ATM is ~ 2 ps with estimated ~ 2 fs resolution. See appendix IV for additional information of the experiment and data sorting.

The experiment was performed with all detectors operating at the full 120 Hz repetition rate of the FEL. In this work, we can explore the behavior of a slower detector by averaging the electron signal over multiple shots.

For linear x-ray/matter interactions, we can model the response of a sample to an incoming x-ray pulse using the linear matrix equation $Ax = b$. Here, x is the time-dependent response of the sample, which we seek to measure. Each row of A is a histogram of x-ray/laser arrival times, weighted by the corresponding x-ray pulse energy, contributing to a single detector frame. The vector b is the electron signal recorded by the electron spectrometer in that detector frame. This is illustrated in figure 2.

In the presence of experimental noise, solving for the sample response function x is non-trivial. We find the vector x that minimizes $\|Ax - b\|_2^2$, subject to additional constraints placed on x according to its known properties. These constraints are enforced using explicit regularization, in which additional terms are included in the objective function being minimized. In the present experiment, we include a regularization term to account for smoothness in the delay-dependent sample response:

$$\|Ax - b\|_2^2 + \lambda \|Lx\|_2^2, \quad (1)$$

where L is the second derivative operator, and the hyperparameter λ is a weighting term which controls the contribution of the regularization term(s) to the total objective function.

In the traditional analysis method of time-resolved photoabsorption spectroscopy, shots within the dataset are sorted into certain delay bins, wherein the electron signal is integrated and normalized to the FEL pulse energy. This traditional analysis can generate a 'ground truth' for detectors recording at the full repetition. This ground truth can be compared to the time-domain ghost imaging reconstruction and for traditional analysis after shot-averaging in the slow detector.

II. RESULTS

Figure 3 shows the delay-dependent sample absorption reconstructed using the technique described above. The results have been produced by grouping different sets of ten shots from the experimental data, to construct the A and b matrices described above. Each panel shows a grouping with different jitter distributions, quoted as a full-width-at-half-maximum (FWHM).

Regardless of the level of jitter, we find that TDGI, shown in blue, produces the same time resolution as the ground truth in black, including the fast rising edge near pump/probe overlap.

The resolution achieved using traditional analysis degrades with increasing delay jitter, as shown by the red line. The overall span of the delay trace is also reduced in the traditional analysis, which is an artifact resulting from the non-uniform sampling of delay points in measurement.

Figure 4 shows the effect of increasing the length of the slow detectors integration window. In this study, we set the FWHM jitter to be 530 fs. For the traditional method (red line), averaging over multiple shots again causes a degradation in the time resolution. The green line shows the results obtained from the TDGI reconstruction for the same averaging window. For 10 and 100 shot averaging windows, the TDGI reconstruction matches the ground truth. However, when averaging over 15 thousand shots, the reconstruction becomes unstable. At these large integration windows, the dataset is reduced to only ~ 5 frames, and all data falls into a single bin and hence the red line corresponding to traditional analysis is completely removed.

The unreliability of the TDGI reconstruction at the selected high integration window is not a limitation of the technique itself, but due to an inadequate volume of data. It is well understood in spectral domain ghost imaging that the quality of reconstruction is dependent on the number of shots acquired [6]. When the system of equations in eq. 1 is highly overdetermined (i.e. there are a large number of shots), the effect of experimental noise can be overcome in the reconstruction of x . Our full dataset is ~ 70 thousand FEL shots, which means for an averaging window of 15 thousand shots, A has only four rows. In this case, 1 becomes highly underdetermined and the reconstruction is unstable. This problem can be overcome by acquiring more data, as we describe below.

To explore the quality of reconstruction as a function of the number of shots in the dataset, we simulate two A matrices for

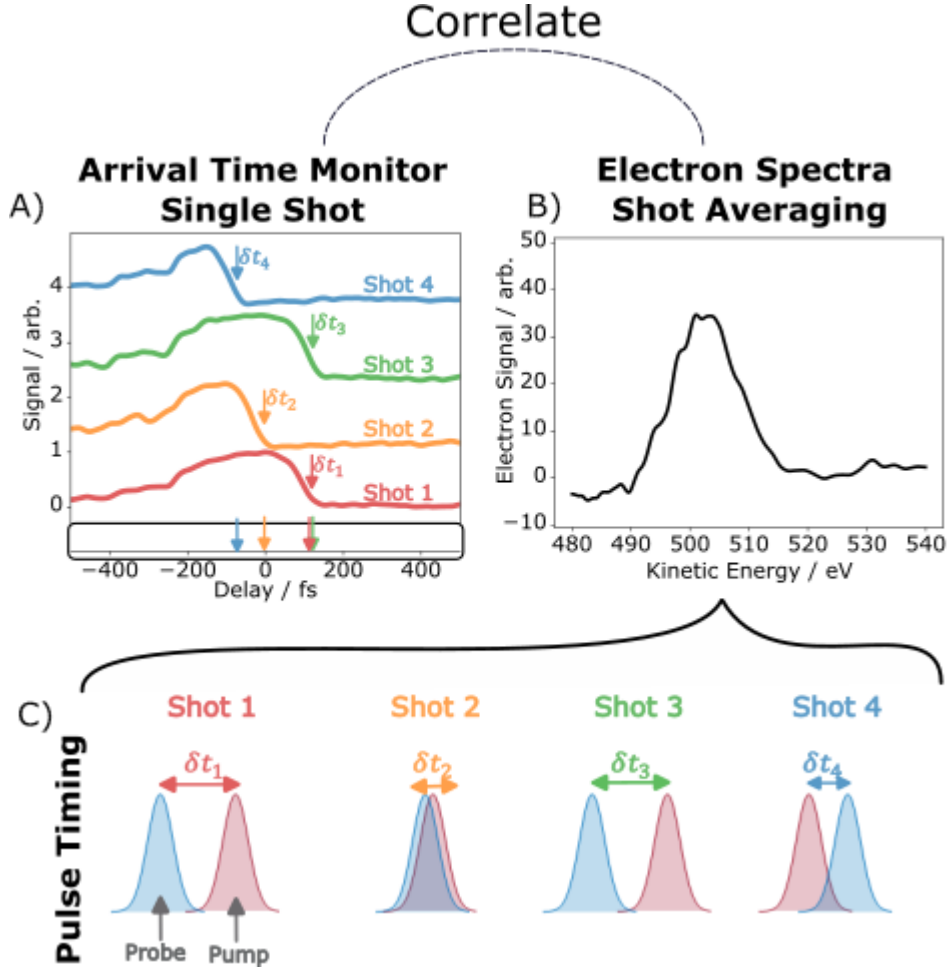


FIG. 1. Schematic representation of our technique. A pump-probe measurement experiences jitter in the pump-probe delay, which is characterized for each shot using a fast detector with an arrival time monitor. A) The pump/probe delay is encoded in the position of the strong modulation in reflectivity of an optical laser which is coincident on a crystal with the FEL pulse. B) The observable of interest is recorded with a slow detector, which averages over multiple shots (bottom row). In our demonstration measurement, the observable is electron yield integrated over kinetic energy region 500–530 eV.

an averaging window of 15 thousand shots. The first A matrix is generated using the same number of shots as our experimental dataset, while the number of shots used to make the second A matrix is larger by a factor of one hundred. The reconstructed results for these two simulated datasets is shown in figure 5. The simulation shows the same unstable behavior observed in figure 4 for a comparable number of shots to the experiment. For the increased data volume, the reconstructed signal again matches the ground truth, as the green line illustrates. This simulation demonstrates that the TDGI method can be implemented even for very large averaging windows, provided an adequate number of shots are recorded. The megahertz repetition rates available from the next generation of XFELs will routinely generate the requisite large volumes of data. See the appendix for more information on simulation methods.

III. OUTLOOK

Thanks to continuously tunable x-ray wavelengths and ultrashort pulse durations, XFELs have proven to be highly useful tools for studying ultrafast phenomena. The next generation of XFELs promise a revolution in experimental capabilities, enabled by high repetition rates which will approach the megahertz regime. Some state-of-the-art detector technology is not yet able to achieve acquisition rates to capture information on a single-shot basis, which leaves measurement resolution vulnerable to the effects of shot-to-shot jitter. In this work, we have demonstrated that the using a fast detector to encode the shot-to-shot jitter in pump-probe delay and correlating this information with a measurement averaged over multiple shots, we are able to recover the same temporal resolution which would be available from a detector running at full beam rate. We have shown that, provided a sufficient volume of data is available, this solution is independent of the degree of jitter and the number of shots over which a detector frame

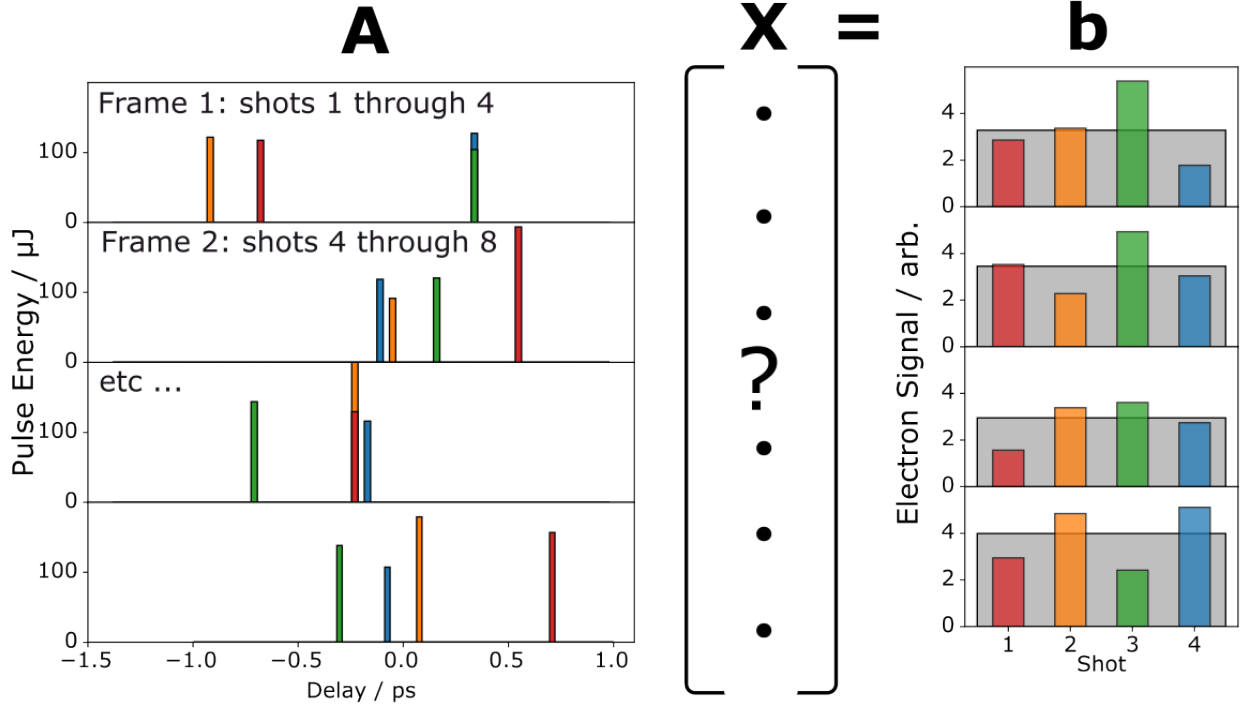


FIG. 2. Representation of the data structures used in TDGI. The A matrix is the distribution of pump/probe delays contributing to a single frame of the slow detector. The vector x is the unknown sample response (in our case, x-ray absorption cross-section) as a function of delay. The vector b represents the electron yield measured in each frame of the slow detector. We solve for x using the method described in the text.

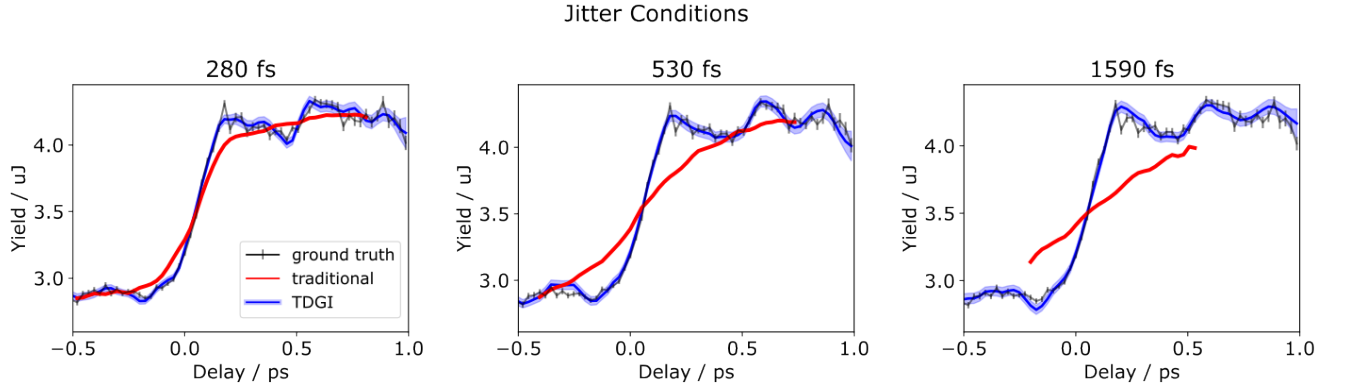


FIG. 3. Recovered delay-dependent signal x for different values of jitter, for a slow detector integration window of ten shots. The time-dependent absorption signal generated using traditional analysis for each set of jitter values is shown in red. The TDGI reconstruction is shown in blue line. TDGI is nearly identical to the ground truth shown in black line. Error bars are generated by standard bootstrapping analysis, as discussed in the appendix.

is averaged. This technique will help realize the full capabilities of the next generation of XFELs, to observe complex molecular dynamics on ultrafast timescales.

IV. APPENDIX

To reconstruct the signal, we employed a quadratic programming optimization package to minimize function 1. This package, written in Python, is freely available online [18]. In

all cases, optimal regularization parameters were selected by employing the L-curve method [20]. The L-curve is a parametric plot of the solution residual against the norm of the solution's laplacian. This curve identifies hyperparameters that lead to under and over-regularization, and regions near the curvature inflection of this plot identify a compromise between overfitting and over-regularization. In the reconstructions shown here, the hyperparameter corresponding to 0.5% of the maximum curvature was selected. However, the solution is robust over several orders of magnitude for λ .

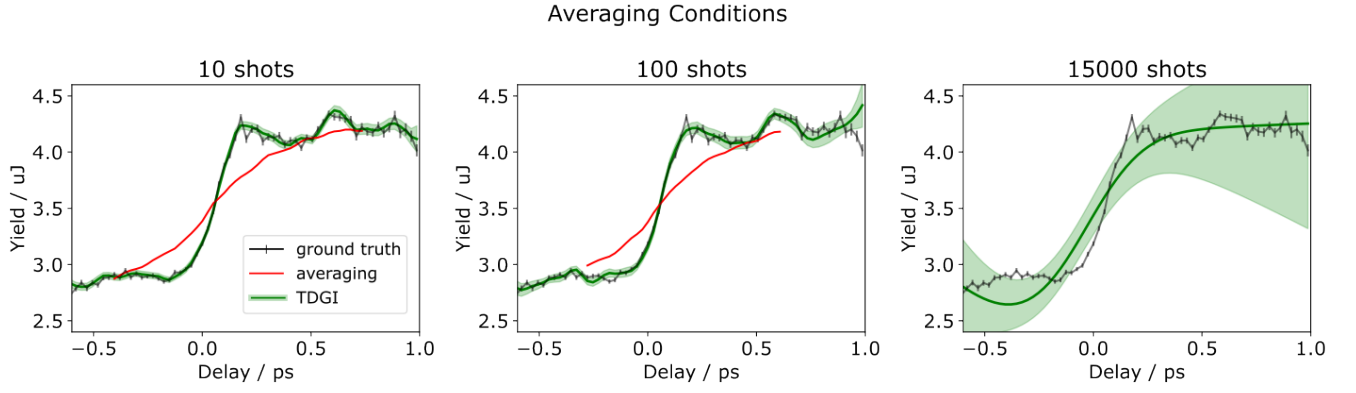


FIG. 4. Recovered delay-dependent signal x for different integration windows and a delay jitter FWHM of 530 fs. The traditional analysis for each set is shown in red. The TDGI reconstruction is shown in green line. TDGI is nearly identical to the ground truth shown in black line. Error bars are generated by standard bootstrapping analysis (see appendix).

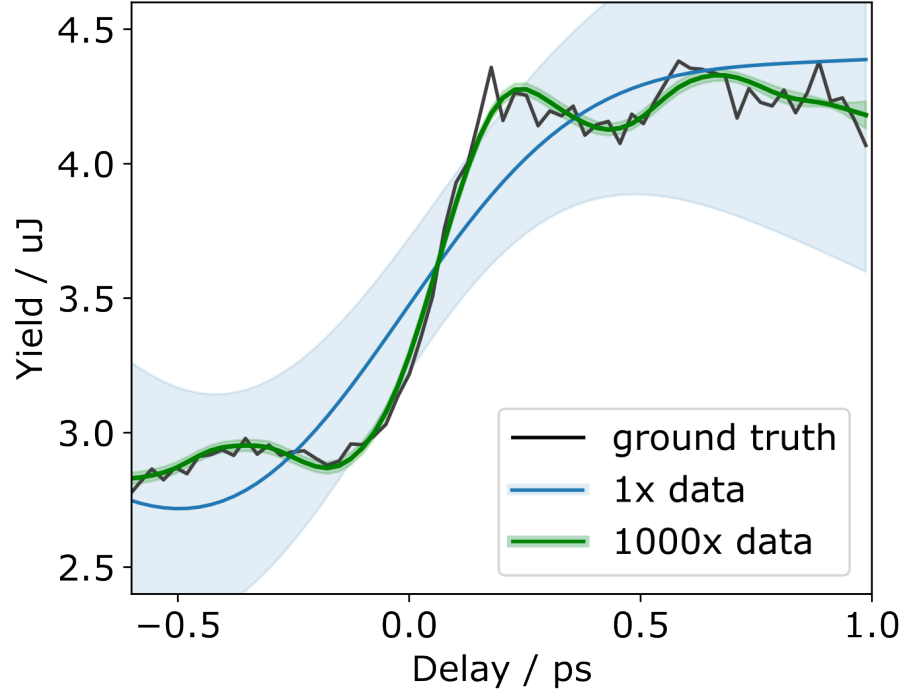


FIG. 5. Effect of increasing data volume on performance of TDGI. Two simulated datasets were generated with the same and 1,000 times the amount of shots in the experimental dataset. Both datasets were averaged over 15,000 shots causes. For the smaller dataset, the TDGI reconstruction becomes unstable, as shown in the blue line. This problem is solved with the larger volume of data, as shown with the green line. Error bars are generated by bootstrapping analysis (see appendix).

Standard bootstrapping analysis was used to determine the uncertainty of the raw non-averaged signal and the reconstructed signal. Datasets A and $\vec{b}$ were randomly resampled with replacement 500 times. The standard deviation across all resamples define the error bars shown in the figures.

The simulated datasets in section II are compiled by randomly generating an reference matrix A . The delay and pulse energy values comprising this matrix were randomly sampled from a normal distribution with the same mean and standard

deviation from the experimental distribution. The x value is the same 'ground truth' discussed in section I, and the b matrix is generated by applying equation $Ax = b$. Random Gaussian noise is applied to the simulated A and b values. The row-entries of A and b are then averaged over 15,000 shots in the same manner as experimntal data, and x is solved for employing the TDGI reconstruction technique.

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Chapter 4

Probing the ring reconfiguration of the quadricyclane-norbornadiene system

This chapter presents the results of experiments studying the ultrafast ring reconfiguration of the isomeric quadricyclane and norbornadiene system. Specifically, results are shown of ultrafast photoelectron spectroscopy to observe the myriad of relaxation pathways of UV-excited quadricyclane. Theoretical results based on complete active space perturbation theory are also discussed.

4.1 Background and Motivation

Carbon ring isomerization occurs in several molecular systems upon UV excitation. Such reactions are common in biological processes, like the ring opening reaction that occurs in photosynthesis³. The binary nature of a ring open/closed geometry may possibly enable molecular logic gates or photoswitches^{87,88,89,90}.

The case of the norbornadiene-quadricyclane (NBD $\rightarrow$ QC) isomerization reaction is a

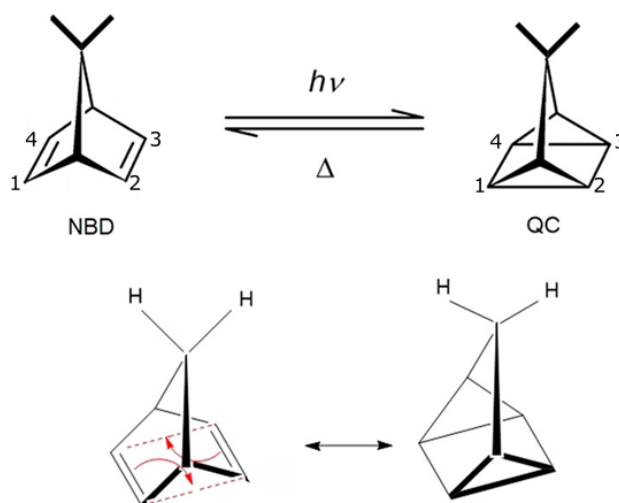


Figure 4.1: Norbornadiene and quadricyclane interconversion. Top: photo or thermal interconversion. Bottom: $[2+2]$ cycloaddition formation to isomerize to QC framework.⁹¹

promising candidate for a molecular photoswitch. The molecules for this isomer pair have the chemical formula C_7H_8 . The molecular geometries are illustrated in the top panel of fig. 4.1. Norbornadiene is a bicyclic molecule, while quadricyclane is a multicyclic molecule in a much more strained configuration. It has been proposed to use this system as a Molecular Optical Solar Thermal (MOST) energy storage solution^{92,93,94}. MOST solutions are designed to initiate an isomerization reaction in a sample upon sunlight absorption. The molecule would go from a less strained to a more strained configuration. The resulting strained product can store the energy gained in this process for hours to years and subsequently release it as usable heat. A schematic of a MOST system is shown in fig. 4.2.

The $NBD \rightarrow QC$ system meets the several criteria for MOST systems, including a highly strained geometry of the QC product and the conversion being reversible. However, the peak absorption of the norbornadiene sits around ~ 200 nm⁹⁶, outside the solar spectral window of 300 to 900 nm. Also, the quantum yield of this isomerization is low, about 5 percent⁹⁴. Lastly, the absorption spectrum of the QC product should have minimum overlap with the NBD precursor, as to avoid any unintended UV-induced reversion.

Several methods to improve the conditions for interconversion have been investigated.

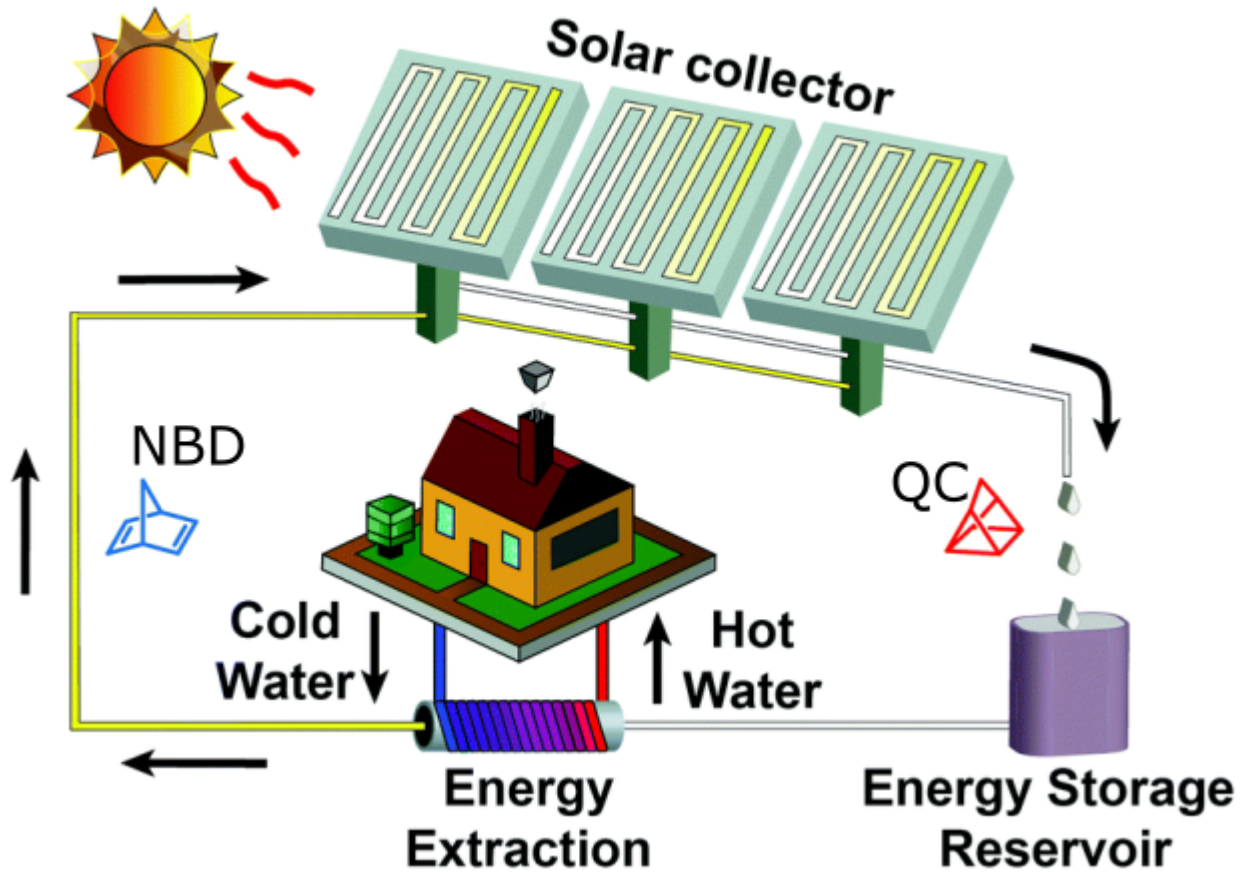


Figure 4.2: Schematic of the MOST concept.⁹⁵

These include site specific donor-acceptor substitutions at the ethylene sites, as well as clustering norbornadiene molecules with bridging catalysts^{97,98,99}. Recent studies have shown that implementing the above methods can significantly redshift the norbornadiene spectrum to values above 300 nm^{100,101,102} and have achieved interconversion quantum efficiency above 50 percent¹⁰³. All these possible applications are dictated by the UV absorption of NBD and interconversion to QC with modified chemical environments or molecular substitutions. It is of interest to understand the fundamental processes of the photoswitch mechanism, including any undesired effect like premature photoconversion from the QC back to the NBD geometry. Thus, we investigate relaxation mechanisms of the UV excited quadricyclane using time resolved photoelectron spectroscopy, a probe that can observe the entirety of the relaxation process to the ground state of both molecules and observe any ultrafast changes in the electronic structure.

The NBD→QC interconversion can be understood as a [2+2] cycloaddition from through-space interaction of the two non-conjugated ethylene pairs as shown in the bottom panel of fig. 4.1. This transition is thermodynamically unfavorable but can be formed photochemically¹⁰⁴. Specifically, after UV-photoexcitation of NBD, a $\pi\pi^*$ transition moves electrons from the region of double-bonding to the region of anti-bonding between the 1 - 2 or 3 - 4 carbon sites.

The photodynamics of this reaction have been studied with 200 nm excitation experimentally with time resolved mass-spectroscopy¹⁰⁵. A valence state is populated, as well as a rydberg state that couples to the valence state via a conical intersection. The wavepacket returns to the ground state through a series of conical intersection and symmetry breaking, with the two ethylenes forming a rhombus. Aside from the Rydberg-valence coupling that had a measured lifetime of 450 fs, all subsequent time constants are very fast, sub- 50 fs, speculating that the barriers to reach the ground state are very small.

Control of the back conversion QC→ NBD through thermal or catalysts methods has been studied extensively⁹⁴. Such mechanisms correspond to the energy release in the MOST

systems. But in photochemistry, QC $\rightarrow$ NBD photoisomerization is also possible^{106,107}. QC has no π orbitals, thus preventing any straightforward pericyclic reaction. From the perspective of electronic structure, photoexcited QC forms a triplet with the same nuclear configuration as photoexcited NBD. Since NBD is the higher-energy isomer, the QC $\rightarrow$ NBD* process would have lower energy requirements than the QC $\rightarrow$ QC* excitation. It's been calculated, that indeed, the barrier energy for ground state QC $\rightarrow$ NBD conversion is 1.47 eV, compared to 2.49 eV for the ground state NBD $\rightarrow$ QC¹⁰⁸. Yet, it has been proposed that the photoisomerization dynamics occur on a manifold of intercoupling Rydberg and valence states. It is these QC excited state dynamics, as well as dynamics occurring upon returning ground state, that this thesis work explores.

Studies of the ultrafast dynamics of excited state quadricyclane have been sparse until recently. Previous studies of the UV induced QC $\rightarrow$ NBD interconversion were performed with a photoelectron spectroscopy technique known as Rydberg fingerprint spectroscopy (RFS) by Rudakov and Weber¹⁰⁹. As with NBD described above, UV excitation of QC populates Rydberg states, molecular states where an electron is excited to such a high lying level that it has little contribution to any chemical bonding and is delocalized. These Rydberg state potential energy surfaces (PES) are often similar to those of the ground ionic state¹¹⁰. The Rydberg states make it such that the binding energy along the Rydberg PES is unvarying with harmonic vibrations or internal temperature in molecular bonds and is more sensitive to changes in a molecule's isomeric or conformic structure and anharmonic vibrations^{111,112}. With this property, the Rydberg electron's binding energy maps to certain geometric configurations, making this electron binding energy a 'fingerprint' for a certain isomer^{113,114,115,116}. These binding energies were determined by measuring the photoelectron kinetic energy from UV probe pulses and using 2.11. Rudakov's work employed a multiphoton pump-probe scheme with a 208 nm excitation pulse, a photon energy 100 meV lower than the experiments discussed in this thesis. Using a traditional electron time-of-flight analyzer with an acquisition rate of 5 kHz, they were able to observe dynamics of the

excited state quadricyclane with three sharp Rydberg peaks and other broad underlying features. By postulating a three step process where a higher lying 3p Rydberg state will relax to a lower lying 3s state, on which the molecule isomerizes to NBD and returns to the ground state, they extracted time constants of 320, 136, and 394 fs for each step. They also observed time-dependent changes in the Rydberg peak positions and narrowing of their widths, which they attribute to the vibrational modes the Rydberg state surfaces becoming more harmonic during relaxation.

Although this experiment revealed the rich time-dependent electronic dynamics, the low energy probe, with photon energy of 3 eV, only allowed for ionizing the excited states. Thus, they could not observe any dynamics associated with relaxation or the hot-ground state, wherein the ground state has several vibrational modes activated due to the energy from the pump pulse. including a broad short-lived feature that was speculated to originate Rydberg-valence coupling after NBD formation¹¹⁷. Understanding any Rydberg-valence or valence-valence dynamics can provide insight to bond lengthening in several molecular systems^{113,118,119}, and subsequent relaxation pathways to the ground state would elucidate nuclear dynamics such as isomerization, e.g., observe hot ground state product QC/NBD ratios. Thus, Rudakov’s work inspired this chapter, which sets out to study the dynamics of the QC/NBD system with experimental techniques that probe any state involved in the relaxation process and aided by more advanced theory.

Specifically, in this chapter, we discuss the results of a time-resolved photoelectron spectroscopy experiment using probing radiation from an XUV FEL at Trieste Italy. This chapter will present published work which discusses the distinct relaxation mechanisms of UV excited QC with interpretation greatly aided by theory. This paper does not include ground state dynamics occurring at longer timescales nor any kinetic fitting models, so such discussions will be included later in this chapter.

4.2 Time-resolved photoelectron spectroscopy of quadricyclane

In this section, we present the results of a time-resolved photoelectron spectroscopy (TR-PES) experiment performed on gas phase quadricyclane. Here, the molecule was excited by a UV pump pulse (201 nm, 6.17 eV), followed by an intense XUV pulse (65.35 nm, 18.97 eV) from the FERMI FEL. The photoelectrons were measured to observe changes in the electron binding energy as a function of pump probe delay. The high photon energy enables single-photon probing at all states occupied during the photochemical reaction, from the excited state to the return on the ground state.

The seeded FERMI FEL provides single-shot stability and narrow bandwidth that are particularly suited for these TRPES experiments. The narrow bandwidth of 24 meV at a central photon energy 18.97 eV provides adequate resolving power to distinguish several nearly overlapping peaks in the photoelectron spectrum. As the FEL pulses are seeded by a high coherent laser pulse, the central photon energy and pulse intensities are stable over long acquisitions. Additionally, as the UV pump pulse is generated from the same laser that generates the seed beam, delay jitter between the UV-pump and XUV-probe pulses is negligible.

The quadricyclane electron binding energy spectra measured with 18.9 eV XUV pulses from the FERMI FEL is shown in fig. 4.3, and superimposed on a high-resolution spectrum from synchrotron radiation, measured 95 eV with an overall resolution of 8.5 meV¹²⁰.

The features in both spectra agree well, with the main difference being the relative peak heights likely due to different ionizing cross-sections between the two different photon energies. For optimal resolution in the high kinetic energy region, the time-resolved data presented later in this chapter was acquired with a retardation of 11V and a 1V pushing voltage applied to the magnet. The ground state spectra under these conditions is shown in red to demonstrate the relative transmission at these low energies after retardation.

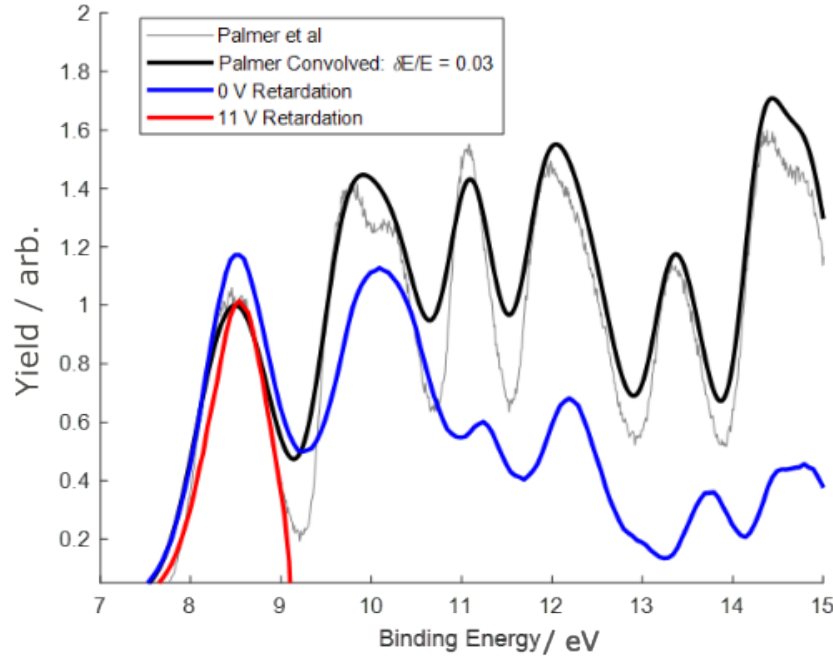


Figure 4.3: Comparison of the photoelectron spectra with high resolution photoelectron spectra from a synchrotron source at 95 eV¹²⁰.

For energy calibration, helium time-of-flight spectra were recorded for different harmonic wavelengths of the seed laser and different retardations. Knowing that the first ionization energy of helium is 24.58 eV, one can determine the kinetic energy by subtracting this binding energy from the known photon energy. As the adiabatic magnetic field of the MBES does not affect the longitudinal direction of electron motion, the central time-of-flight peak can be fitted to the kinetic energy by the kinetic equation

$$KE = \frac{C^2}{(t - t_0)^2} + R, \quad (4.1)$$

where the fit parameters relate to the spectrometer length (C), energy offset from retardation and magnet push (R), and the FEL pulse onset time relative to the digitizer (t_0). The electron binding energy of QC was then determined by subtracting this calculated kinetic energy from the known photon energy: $BE = \hbar\omega - KE$, using all the assumptions discussed in section 2.3.

To assure the dynamics induced by the UV pump pulse were the single-photon processes we intended to study, the photoelectron spectrum were recorded with different UV pulse energies at a single delay, as shown in fig. 4.4. Panels A and B show the difference signal (spectra recorded with UV off subtracted from spectra with UV on) in the excited state enhanced region and the ground state depletion region, respectively. Features in these spectra seem qualitatively similar for each pulse energy. Panels C and D show the electron yield for the same regions integrated over different binding energy bins. In the excited state shown in panel C, the linear relationship signifies a single-photon processes holds until $\sim 14 \mu\text{J}$ before saturating.

For the ground state region shown in panel D, the deviation from the linear regime is more apparent at approximately $11 \mu\text{J}$. At the excitation photon energy of 6.17 eV , only two UV photons are needed to ionize the molecule (with binding energy of 7.8 eV), and multiphoton effects will appear as bleaching of the ground state. Data shown in this work is primarily taken at $10 \mu\text{J}$ pulse energy.

4.2.1 Ultrafast electronic dynamics of UV-excited quadricyclane

This study aims to elucidate the ultrafast relaxation pathways in quadricyclane after UV excitation and does so by time resolved measurements with ab initio molecular simulations.

Quadricyclane molecules were excited through the absorption of a single UV photon, and subsequently ionized by an XUV photon from a seeded FEL. Figure 2 of the following paper shows the measured time-resolved photoelectron spectra, wherein several distinct features are present. Near time-zero pump-probe overlap, the features corresponding to the ground state spectra are depleted as a sizable population is excited to higher lying states, as evident in the signal enhancement at smaller binding energies. In this excited state region, narrow-band discrete features survive until over 300 femtoseconds. These features are attributed to long lived Rydberg-states. Lying under these features is a broad-band feature that is very short lived and belongs to the valence states. Combining these experimental results

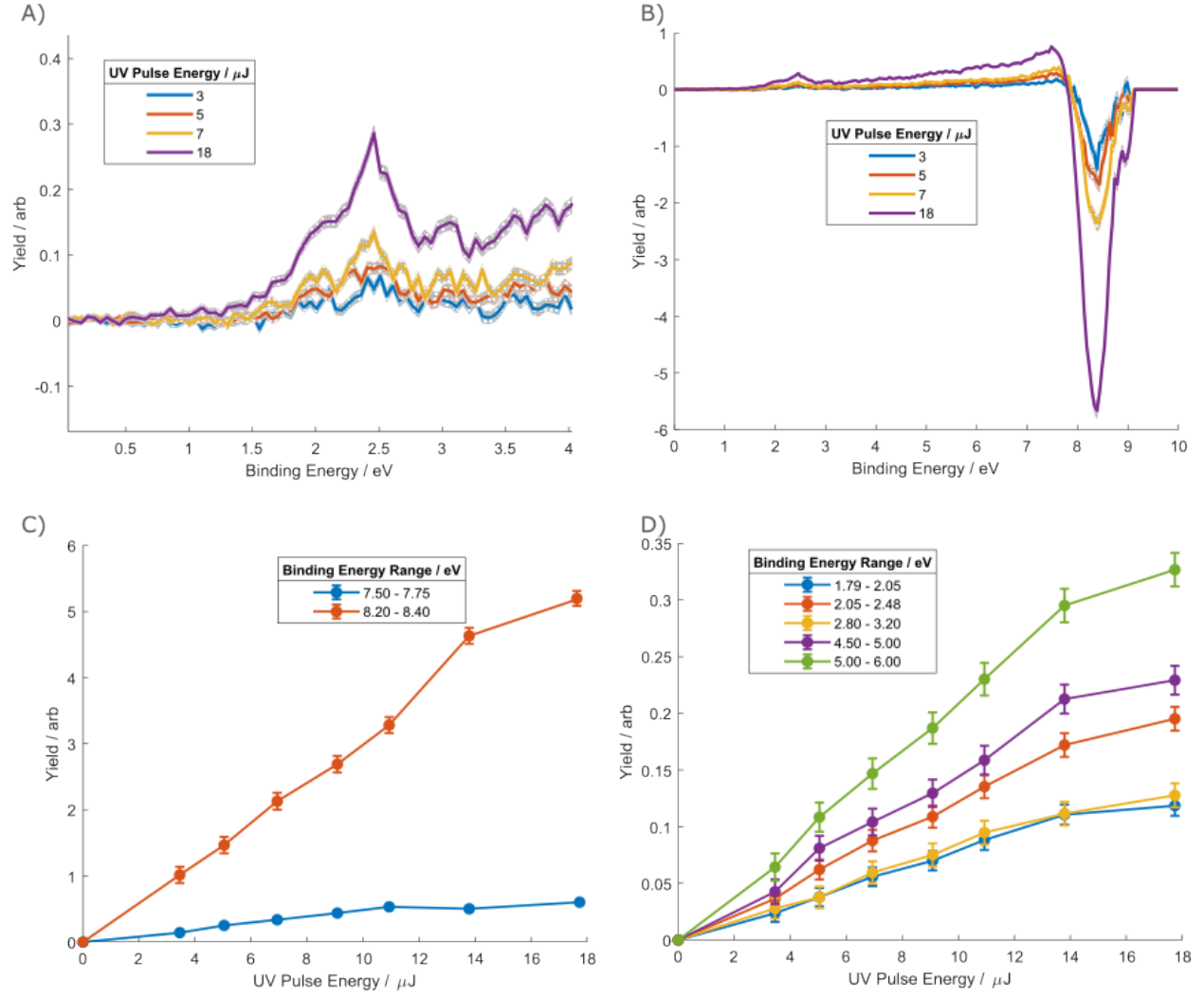


Figure 4.4: UV fluence-dependence of the pump-probe signal. A) Photoelectron spectra with subtraction of the “UV-off” signal for QC in the excited-state region at different UV pulse energies at a pump-probe delay of 0.5 ps. B) Same as (A) but shown for the entire binding energy range. C), D) Integrated electron yield for different binding energy regions as a function of UV pulse energy.¹⁹

with theoretical calculations, we can understand how these relaxation pathways facilitate isomerization to the norbornadiene product.

Clear experimental evidence as to what states were populated helped guide the theoretical calculations. The electronic structure calculations were performed using CASPT methods for both the neutral and the ion¹²¹. The complete active space contained the 3s and 3p Rydberg states and two valence states. Nonadiabtic trajectories, 267 in total, were ran using a surface-hopping method¹²², and only the first five excited states were included. Initial states were prepared with 45% on the S2 and 55% on the S3 and S4, this selection was guided by the calculated partial absorption cross-sections. The results of the trajectory calculations were split into two different features, a fast valence and slow Rydberg, with results showing a similar isomerization fraction to NBD on both pathways, albeit different timescales, as shown in figure 4 of the attached paper.

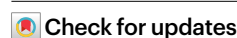
These calculations were performed by author Joseph Cooper with guidance from Adam Kirrander.

Ultrafast electronic relaxation pathways of the molecular photoswitch quadricyclane

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The light-induced ultrafast switching between molecular isomers norbornadiene and quadricyclane can reversibly store and release a substantial amount of chemical energy. Prior work observed signatures of ultrafast molecular dynamics in both isomers upon ultraviolet excitation but could not follow the electronic relaxation all the way back to the ground state experimentally. Here we study the electronic relaxation of quadricyclane after exciting in the ultraviolet (201 nanometres) using time-resolved gas-phase extreme ultraviolet photoelectron spectroscopy combined with non-adiabatic molecular dynamics simulations. We identify two competing pathways by which electronically excited quadricyclane molecules relax to the electronic ground state. The fast pathway (<100 femtoseconds) is distinguished by effective coupling to valence electronic states, while the slow pathway involves initial motions across Rydberg states and takes several hundred femtoseconds. Both pathways facilitate interconversion between the two isomers, albeit on different timescales, and we predict that the branching ratio of norbornadiene/quadricyclane products immediately after returning to the electronic ground state is approximately 3:2.

Molecular photoswitches are an exciting area of research with emerging applications in catalysis, photochromic materials, molecular machines, logic devices and energy storage¹. The last example includes molecular solar thermal (MOST) energy storage solutions, whereby molecular

isomers are exploited to absorb, store and later release solar energy as heat^{2,3}. An important model system for such applications is the photoswitchable pair of isomers quadricyclane (QC), a highly strained multicyclic hydrocarbon, and its lower-energy isomer norbornadiene (NBD)^{4–9},

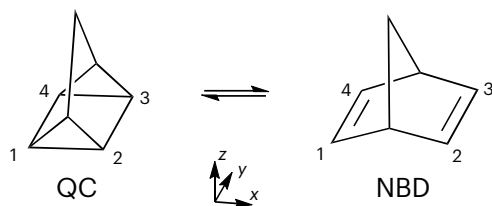


Fig. 1 | Schematic of the QC $\rightleftharpoons$ NBD interconversion. The isomerization reaction breaks (or forms) the 1–2 and 3–4 carbon–carbon bonds in QC, with the energy of the QC ground state located ~ 1 eV above the ground state of NBD. The interconversion can be driven by light absorption, allowing the system to act as a molecular photoswitch.

whose International Union of Pure and Applied Chemistry (IUPAC) names are tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (QC) and bicyclo[2.2.1]hepta-2,5-diene (NBD). The isomers, shown in Fig. 1, interconvert upon photoabsorption in the ultraviolet (UV) range^{10–13}. More broadly, the photoisomerization of NBD $\rightarrow$ QC is an example of a [2 + 2] cycloaddition reaction, and the behaviour of the molecule is reminiscent of the prototypical ethylene dimerization, with the bridging framework acting to hold the ethylene moieties together^{14,15}. We investigate the mechanism of the reverse interconversion, QC $\rightarrow$ NBD, which is of both fundamental photochemical interest and practical importance since it represents the undesired UV-induced photoreversion process in QC/NBD-derived MOST systems.

Early time-resolved ion mass spectrometry experiments on gas-phase NBD noted signatures of ultrafast molecular dynamics upon UV excitation at 200 nm (6.20 eV), which were speculatively attributed to transitions from a superposition of Rydberg and valence states to the electronic ground state via a series of conical intersections on a sub-100 femtosecond timescale¹⁵. A subsequent study on QC excited at 208 nm (5.96 eV) employed time-resolved Rydberg fingerprint photoelectron spectroscopy¹⁶. The latter work suggested that QC isomerizes to NBD on the 3s Rydberg state within 140 fs and that relaxation to the electronic ground state occurs within 400 fs. Notably, that study could not observe the dynamics all the way to the ground state since the probe photons had insufficient energy to ionize ground-state molecules. Theoretical work has focused on the photorelaxation of NBD, examining the electronic structure^{4,9,17} and the dynamics^{18,19}. In both cases, the key role of interactions between the Rydberg manifold and valence states in NBD was highlighted.

In the present study, we use time-resolved photoelectron spectroscopy (TRPES) with extreme ultraviolet (XUV) probe pulses, capable of tracking the entire reaction path from the initial UV-excited states through to the electronic ground states of both isomers. TRPES with XUV pulses is a powerful method for mapping complex chemical dynamics^{20–24}. Our experimental data, supported by high-level simulations, provide a much more complete description of the deactivation mechanisms in QC, thus providing mechanistic insights that can be used to design more-efficient MOST systems.

Results

We initiate the photochemical reaction in gas-phase QC by a UV excitation pump pulse at 200.6 nm (6.18 eV), followed by an XUV ionization probe pulse at 18.97 eV (65.35 nm) from a seeded free-electron laser (FEL). The TRPES spectra obtained as the difference between the spectra acquired with and without the pump pulse (Methods and Supplementary Section 1.4 for details) are shown as a two-dimensional false-colour map in Fig. 2a. One-dimensional spectra obtained by averaging over selected time-delay ranges are displayed in Fig. 2b,c (additional spectra are shown in Extended Data Fig. 2). Several prominent features are apparent. A narrow and long-lived feature at ~ 2.3 eV binding energy (BE), visible as a faint horizontal line in Fig. 2a and as a clear peak in Fig. 2b, is assigned to two of the three 3p Rydberg states of QC

in accordance with the literature¹⁶. The 3s Rydberg state can be seen at a BE of ~ 2.9 eV in Fig. 2b but has a weaker signature than in earlier studies¹⁶, suggesting less excitation to the 3s state at 200.6 nm compared to 208 nm. Figure 2a also shows a spectrally broad and short-lived vertical feature in the BE range of ~ 1.5 –7 eV, which merges into a long-lived horizontal band at ~ 7 –8 eV BE, both of which were not observed in the earlier work that did not have a sufficient photon energy to ionize this BE region. These observations suggest the existence of a rapid (<100 fs) deexcitation pathway leading to the formation of vibrationally hot photoproducts, while the longer timescale of the Rydberg-associated features indicates the existence of a second, slower decay mechanism, which corresponds to the pathway identified in earlier work¹⁶. Finally, there is a pronounced negative signal in the difference spectrum in the BE range 8–9 eV, assigned to the depletion of the QC ground state, followed by a partial recovery.

Delay-dependent photoelectron yields in selected spectral regions are shown in Fig. 2d,e. They display a nearly Gaussian shape at low BE values with a temporal width that is mostly given by the instrument response function (Methods), while clear exponential ‘tails’ are visible in the range of the Rydberg excitations and in the high-BE yields. Least-square fits of the delay-dependent yields are provided in Supplementary Figs. 9–11.

The nature of the previously unreported broad, short-lived feature with BE values in the range ~ 1.5 –7 eV is investigated further using high-level electronic structure calculations and non-adiabatic dynamics simulations. Figure 3 shows calculated potential energy curves for the ground (S_0) and first five singlet excited (S_1 – S_5) electronic states identified as being active in the dynamics probed by the present experiment, plotted along a linear interpolation in internal coordinates (LIIC) from the equilibrium geometry of QC(S_0) to the S_1/S_0 minimum energy conical intersection (MECI) and then continued along a second LIIC from this MECI to the NBD(S_0) equilibrium geometry. The dominant electronic characters and adiabatic energies at the equilibrium geometries and the MECI are given in Table 1. In the Franck–Condon (FC) region of QC, the S_1 adiabatic state has 3s Rydberg character; S_3 and S_4 are 3p Rydberg states; and S_2 and S_5 are a pair of mixed 3p_x/valence (V) states. As the QC molecule approaches the MECI geometry, the S_1 state acquires valence character, which persists into the FC region of NBD. A complete discussion of the vertical electronic spectra of both isomers, complementing the work by Palmer et al.^{17,25}, is reserved for a separate publication²⁶.

Discussion

The potential energy curves in Fig. 3 suggest the possible mechanisms that underpin the features observed in the TRPES data, with the two pathways indicated schematically by black arrows. From the QC ground state, the bandwidth of the pump pulse (0.6 nm) allows excitation to a manifold of closely spaced states with 3p Rydberg character (Extended Data Fig. 7). Population in the 3p_{y/z} Rydberg states (S_3 and S_4 in the FC region) then evolves via a (comparatively) slow Rydberg pathway on the rather flat Rydberg manifold at excitation energies of ~ 6 eV; we anticipate that this would correspond to the pathway observed previously¹⁶. Due to the similar topographies of the Rydberg and ground-state ion (D_0) adiabatic potential energy surfaces, the BE values for the slow Rydberg pathway can be expected to be relatively constant—as observed experimentally. Conversely, in the fast valence pathway, the population in the strongly mixed Rydberg–valence 3p_x/V state (S_2 in the FC region) is subject to efficient non-adiabatic coupling to S_1 , funnelling down towards a conical intersection with the S_0 state. In the proposed model, the BE values for the fast valence pathway would increase rapidly, consistent with the short-lived structure observed for experimental BE values in the range of ~ 1.5 –7 eV.

We confirm these hypothesized mechanisms using non-adiabatic mixed quantum–classical trajectory simulations (Methods). The simulations divulge that the photodynamics of excited QC are strongly

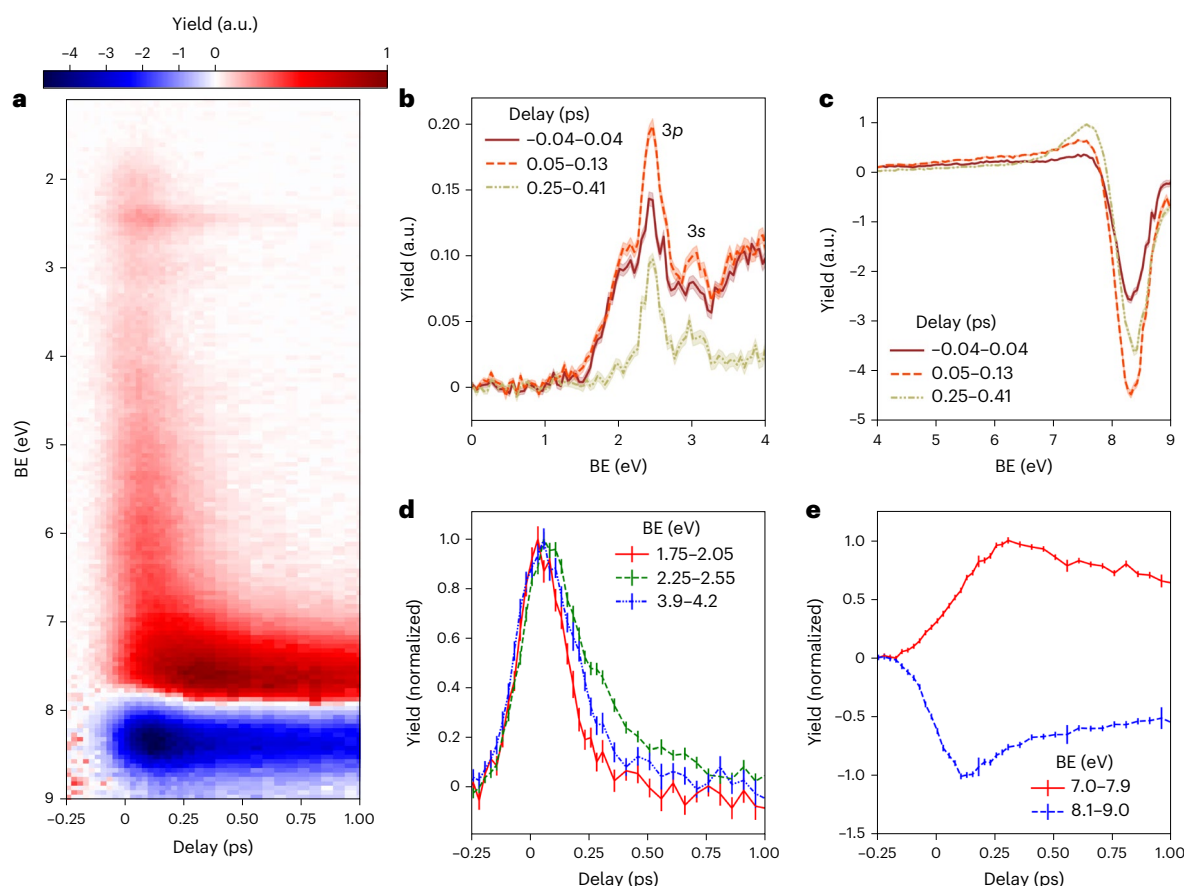


Fig. 2 | Experimentally measured TRPES spectra of UV-excited QC.

a, Photoelectron spectra as a function of BE (with respect to the first ionization potential, D_0) and pump–probe time delay between UV and XUV pulses, plotted as the electron yield difference between spectra taken with and without the UV-excitation pulse (Extended Data Fig. 1). The respective electron yield at each delay is normalized to the FEL pulse energy before subtraction, and the difference signal is normalized to the integrated electron yield without UV excitation, both summed over all shots at the respective delay. Negative

delays correspond to the FEL pulse preceding the UV excitation pulse.

b,c, Photoelectron BE spectra in the excited-state region (**b**) and at large BE values that sample the electronic ground state (**c**) at specific time delays.

d,e, Delay-dependent electron yield in the denoted BE regions, normalized to have the same peak amplitudes. The data and error bands (shading) in **b** and **c**, and the error bars in **d** and **e**, represent the mean value of approximately 40,000 single-shot digitizer traces and the 68% confidence interval obtained from a bootstrapping analysis (Methods).

dependent on the initial excited state. Figure 4 shows the results separated into two sets. Dynamics initiated on the S_2 ($3p_x/V$) state are labelled fast valence, shown in the top row, while dynamics initiated on the S_3 and S_4 ($3p_y$ and $3p_z$) states are labelled slow Rydberg and shown in the bottom row. The plots in Fig. 4a show false-colour maps of the nuclear dynamics along the coordinate associated with the making and breaking of the 1–2 and 3–4 carbon–carbon bonds (r_{12} and r_{34} , respectively) during the interconversion between QC and NBD (Methods). The left and right sides show the trajectories on the excited states and ground state, respectively. Figure 4b shows the time-dependent electronic-state populations and the fraction of population best defined as NBD-like, while the false-colour maps in Fig. 4c finally show the contributions to the simulated TRPES spectrum to aid comparison with the experimental data in Fig. 2a.

We first examine the simulation results for the fast valence mechanism shown in the top row of Fig. 4, corresponding to trajectories initiated on the S_2 ($3p_x/V$) state. One-photon excitation to the $3p_x/V$ state from the S_0 state is symmetry forbidden at the exact equilibrium geometry, but the transition gains strength from the Herzberg–Teller effect (45% excitation fraction; Methods). The nuclear dynamics in the electronic excited states (Fig. 4a, left side) break the carbon–carbon bonds along r_{12} and r_{34} , allowing the molecule to deform towards NBD-like geometries ($r_{CC} = (r_{12} + r_{34})/2 > 2.0$ Å). The wave packet then returns

towards QC-like geometries (smaller r_{CC}) and crosses to the S_0 ground state via a conical intersection, appearing on the right side. It immediately partitions into QC-like and NBD-like geometries. The recurrences in the upper map reflect the persistence of the ‘butterfly’-like vibrational motion of the NBD products when they first reach the S_0 state (with wave number $\tilde{\nu} \approx 428$ cm^{-1})²⁷. The corresponding motion in QC has a higher wave number ($\tilde{\nu} \approx 721$ cm^{-1})²⁸ but can also be discerned in the lower maps.

This picture is confirmed in the upper plot of Fig. 4b, which shows almost immediate population transfer from S_2 to S_1 via internal conversion (zoomed-in view in Extended Data Fig. 6), followed by another rapid internal conversion to S_0 , with only a small fraction (<10%) of the population remaining in the Rydberg manifold after 1 ps. The time-dependent fraction of molecules with NBD-like geometries (that is, with $r_{CC} > 2.0$ Å) in the same graph shows a rapid early increase and then decline (mirroring the S_1 state population), finally converging to a branching ratio of ~3:2 for NBD-like to QC-like geometries in the S_0 state. This ratio is set by the decay dynamics rather than energetics, as the timescales are far too short for thermalization on the ground state.

The theoretically predicted TRPES signal in Fig. 4c shows a curved band of intensity evolving from the BE values of the Rydberg state (~2.1 eV) down to that of the S_0 state (~7 eV), in good accord with the ‘hockey-stick’-shaped feature in the experimental data (Fig. 2a). In

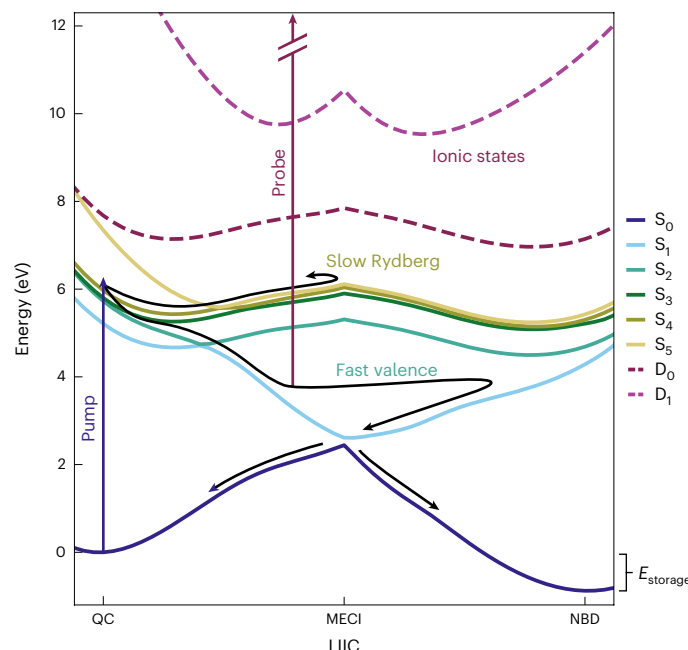


Fig. 3 | Potential energy curves for QC and NBD along the LIICs. Potential energy curves for the ground state S_0 and excited states S_1 – S_5 , as well as the cation ground state D_0 and first excited state D_1 (dashed lines), calculated along the LIICs, first from QC to the S_1/S_0 MECI and then from the MECI to NBD, using RMS-CASPT2(2,6)/6-31G* + D (Methods and Supplementary Section 2.1). The two proposed reaction pathways are indicated schematically by black arrows, with the slow Rydberg pathway supporting vibrational motions on the Rydberg states before relaxing via the S_1 state, while the fast valence pathway descends on S_1 , bypassing the MECI on the initial descent, before crossing onto the S_0 ground state to form both products. The molecular geometry at the MECI has a distinct rhombic distortion (Extended Data Fig. 3). The E_{storage} indicates the energy stored in QC relative to NBD (–1 eV). Corresponding vertical excitation energies are listed in Table 1, and a plot including higher excited states and the approximate state characters is provided in Extended Data Figure 4.

part, this broad feature reflects the very fast motion of the wave packet down the $3p_x/V$ surface, with a corresponding rapid increase in the BE with respect to D_0 . In addition, there is a smaller contribution from the D_1 ionization channel when the wave packet approaches the MECI. Figure 4a (upper left map) shows that the bond breaks and reforms in under 100 fs, faster than the instrument response function of the experiment, making these features appear almost simultaneously at time $t = 0$. A more detailed analysis of the components of the photoelectron signal is provided in the Supplementary Information.

Next, we consider the slow Rydberg pathway with trajectories initiated on the $S_{3/4}$ ($3p_{y/z}$) states, shown in the bottom row of Fig. 4. Already on the left side of Fig. 4a, it is apparent that the excited-state dynamics persist for substantially longer than in the fast valence mechanism, and that the dynamics are more centred at QC-like molecular geometries ($r_{\text{CC}} < 2.0$ Å), with only a small fraction of the trajectories exploring NBD-like geometries in the $3p$ excited states, discernable as a faint signal at $r_{\text{CC}} > 2.0$ Å. Examining the populations in Fig. 4b, we see a comparatively slow but steady deactivation of the Rydberg manifold states (S_2 and higher) with a matching increase in S_0 population. The decay proceeds via the same $3p_x/V$ state as the fast valence mechanism, evidenced by the build-up of population in the S_1 intermediate state, which acts as a funnel towards the S_0 state via the conical intersection. It appears that this conical intersection has a strong influence on the NBD/QC branching ratio in the S_0 state, since the fraction of NBD (Fig. 4b, bottom) approaches the same value as the fast valence pathway.

The simulated TRPES signal in Fig. 4c shows a long-lived feature with BE ≈ 2.1 eV, corresponding to the $3p$ Rydberg states (with potentials

Table 1 | Vertical excitation energies for each of the five excited singlet states, labelled S_1 – S_5 , with the dominant electronic character provided in parentheses, as well as the $S_0 \rightarrow D_0$ ionization potential at the respective equilibrium geometries of QC and NBD and at the S_1/S_0 MECI geometry, calculated using RMS-CASPT2(2,6)/6-31G* + D

State	QC (eV) (character)	MECI (eV) (character)	NBD (eV) (character)
S_1	5.29 (3s)	0.00 (V)	5.25 (V)
S_2	5.82 ($3p_x/V$)	2.74 (3s)	5.61 (3s)
S_3	5.88 ($3p_y$)	3.31 ($3p_x$)	6.11 ($3p_y$)
S_4	6.05 ($3p_z$)	3.47 ($3p_y$)	6.28 ($3p_x$)
S_5	7.53 ($3p_x/V$)	3.53 ($3p_z$)	6.34 ($3p_z$)
IP ($S_0 \rightarrow D_0$)	7.67	5.26	8.02

Note that the numbering of the states is directly related to the electronic structure model used. The geometries are shown in Extended Data Fig. 3. The value of the average carbon–carbon distance coordinate r_{CC} for the three geometries is $r_{\text{CC}}^{\text{QC}} = 1.51$ Å, $r_{\text{CC}}^{\text{MECI}} = 1.98$ Å and $r_{\text{CC}}^{\text{NBD}} = 2.47$ Å. At the QC ground-state geometry, in the two mixed states S_2 and S_5 , the $3p_x$ component is dominant in S_2 and the valence (V) component is dominant in S_5 .

along the LIIC of interest that closely track that of the D_0 ionic state), in good accord with the experimental data, which show the corresponding feature attributable to ionization from these Rydberg states at BE ≈ 2.3 eV (Fig. 2a). At long times, the TRPES signal seen in the slow Rydberg and fast valence dynamics are essentially identical. Both pathways involve similar ultimate decays to the S_0 state, yielding similar branching ratios of hot QC and NBD products. Note that the vertical ionization potentials of QC and NBD are similar, differing by ~ 0.3 eV (Methods). Thus, the TRPES signals of hot ground-state QC and NBD species overlap, and the experimentally observed bleach recovery in Fig. 2e includes components from both isomers.

Notwithstanding the very good agreement between experiment and theory, some discrepancies are evident. The simulations return longer Rydberg state lifetimes than observed experimentally, which could reflect shortcomings in the electronic structure theory, for example, regarding the strength and location of the couplings with the $3p_x/V$ state, additional decay paths not accounted for by the active space used or the accuracy of the predicted ionization cross-sections.

In summary, TRPES studies using XUV photons from a seeded FEL have provided new and detailed insights into the relaxation pathways of electronically excited QC molecules formed by photoexcitation at 200.6 nm, from Rydberg states through to vibrationally excited hot ground-state QC and NBD molecules. We present observations of the dominant relaxation pathway in QC, involving strong Rydberg–valence coupling, alongside the previously observed Rydberg-state-mediated isomerization¹⁶. The present combined experimental and theoretical study shows that all three $3p$ Rydberg states of QC are excited by the 200.6 nm pump pulse. The lowest-energy ($3p_x$) state is strongly coupled to a valence state, giving rise to the fast valence pathway characterized by ultrafast electronic decay and nuclear motion. The other two support initial nuclear dynamics in the Rydberg manifold, prior to comparatively slower decay to the ground state (identified here as the slow Rydberg pathway). The simulations suggest that $\sim 40\%$ of the vibrationally excited ground-state products sampled at pump–probe delays of ~ 1 ps correspond to QC-like structures, irrespective of the decay pathway followed, and that this early-time partitioning is determined by the molecular dynamics rather than thermodynamics.

The insights provided by the present study point to key features that affect the photodynamics: the partial absorption cross-sections, the strength of the non-adiabatic couplings to the valence excited state

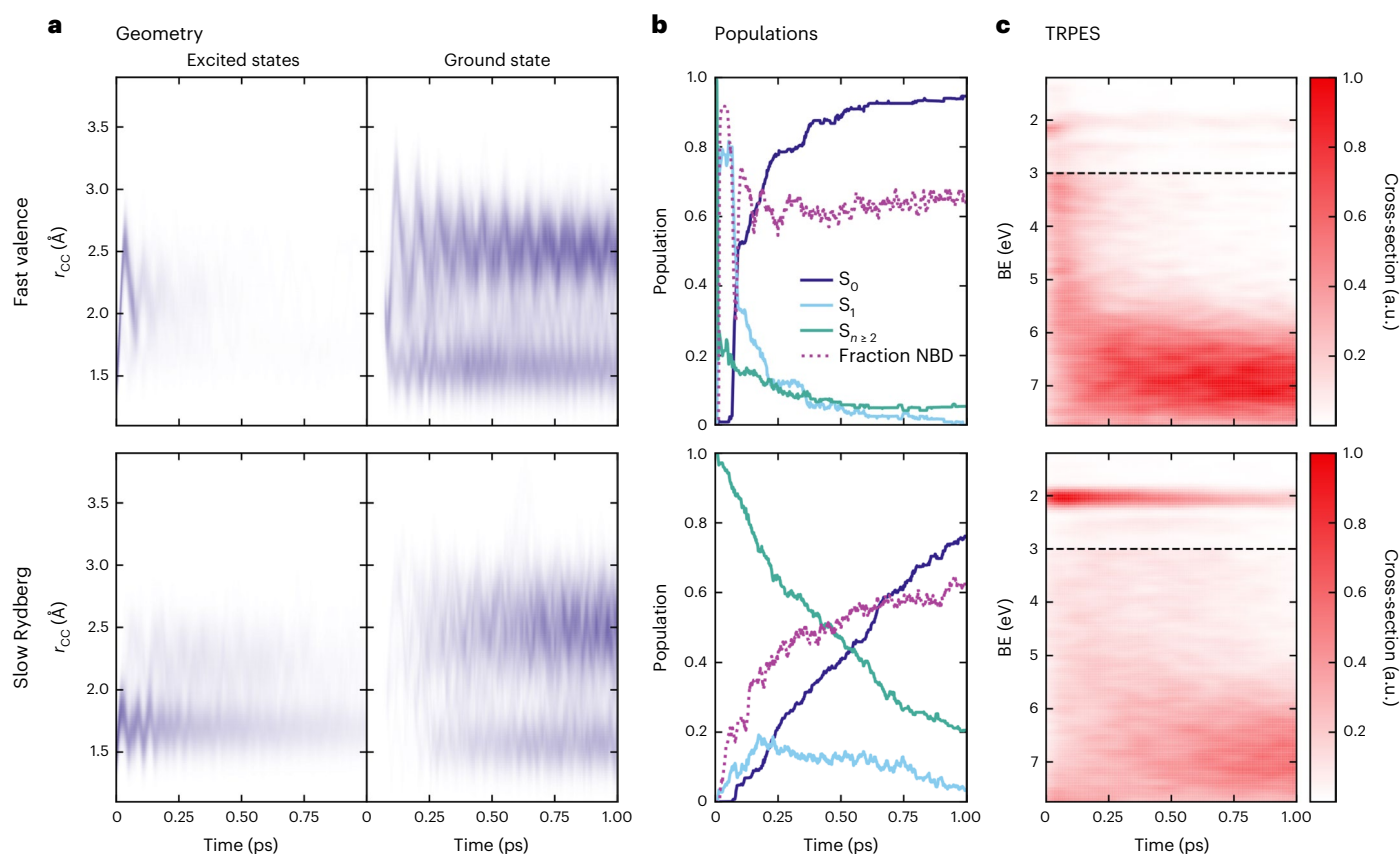


Fig. 4 | Simulated dynamics of UV-excited QC. The simulations are separated into the fast valence mechanism (top row, corresponding to trajectories starting on the S_2 state) and the slow Rydberg mechanism (bottom row, trajectories originating on the $S_{3/4}$ Rydberg states). A zoomed-in depiction of the first 200 fs is shown in Extended Data Fig. 6. **a**, False-colour maps for average carbon–carbon distance $r_{cc} = (r_{12} + r_{34})/2$ versus time (Methods). The left and right sides show the nuclear dynamics in the excited states and the ground state (S_0), respectively.

b, Populations of the electronic states as a function of time, where $S_{n \geq 2}$ shows the cumulative population of the excited states other than S_1 . These plots also show the fraction of molecules with NBD-like geometry (defined as $r_{cc} > 2.0$ Å). **c**, Simulated TRPES data, convoluted by Gaussian functions with full-width at half-maximum of 0.1 eV and 94 fs. Signals with BE > 3 eV (below the horizontal dashed line) have been multiplied by a factor of three prior to display.

and the relative stabilities and geometries of the regions of maximal interstate coupling, that is, the conical intersection between the S_1 and S_0 states. For potential applications, these properties could be manipulated using substituent groups, using spatial confinement and/or by the choice of excitation wavelength^{5,8,19,29}. For instance, the detailed nature of valence/Rydberg mixing in the valence state controls its energy and accessibility, which could be used to affect the system's function as a molecular photoswitch. The manner in which the wave packet approaches the S_1/S_0 conical intersection region is also important, and this could be manipulated either in the preparation of the wave packet or by altering the position and shape of the conical intersection.

From a broader photochemical perspective, one might conjecture that the bipartite dynamics found here will be a common feature whenever a manifold of Rydberg states intersects valence states in the FC region^{30–32}. The excitation energies to Rydberg states typically fall within ~3 eV of the associated ionization limit, E^{IP} (IP, ionization potential), and, in most small to medium-sized molecules, will overlap with those of one or more excited valence states. Rydberg excitations will manifest as a longer-lived trapping component, whereas excitations to valence states (or, as here, to a mixed Rydberg–valence state) will lead to more-rapid relaxation that gives rise to broad features in the photoelectron spectrum. Broadband excitation can excite both types of states, leading to both types of mechanism. Bifurcation of wave packets has been reported previously, for example, in the photoisomerization

of stilbene³³ and in photoexcited inverse dithienylethene derivatives³⁴, but in most such cases studied hitherto, the bifurcation arises as a result of sampling a ‘transition-state’-like region of a common excited state (for example, a $\pi\pi^*$ state), the potential energy surface of which supports multiple minima.

The current results demonstrate the utility of TRPES with XUV probes for characterizing complex photochemical mechanisms. Comparison with previous experiments¹⁶ indicates that a systematic examination of the effect of excitation wavelength would be useful. Ideally, this should be coupled to complementary experimental work more sensitive to molecular geometry. For instance, ultrafast electron diffraction and ultrafast X-ray scattering experiments^{35–38} might offer further insights into the dominant conical intersection and, at longer times, reveal fragmentation products from the hot ground-state molecules. We anticipate that future experiments should provide an even deeper understanding of the intriguing ultrafast ring reconfigurations in this photoswitch molecule.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41557-023-01420-w>.

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4.2.2 Analysis of decay pathways and excited-state kinetics

To extract quantitative information from the measured time-resolved photoelectron spectra we can apply a kinetic fitting model¹²³. These models are generally used to extract timescales of chemical reactions, as they relate the rate at which a reaction occurs depending on the concentrations of a statistical ensemble. Fitting to these kinetic models may help us disentangle overlapping features in the experimental spectra, such as any intermittent species throughout the QC to NBD isomerization. These fits help us extract timescales and the weights of contributing features to determine what is the dominating mechanism in the photochemical process. Although the theoretical simulations have provided good qualitative agreement to the experiment, several features could be missed due to limitations in the theory, especially the limited selection of states in the active space used to propagate the dynamics. Additionally, if the predicted ionization cross sections from theory are inaccurate, it may not accurately determine the contribution of those states to the final observable for comparison with experiment.

The excited state region of the TRPS contains several features all occurring within a short timescale. Hence, in this region we perform decay associated spectroscopy (DAS)^{124,125,126}, a global fitting procedure that is capable of modelling all the contributing photoelectron signals simultaneously. DAS accomplishes this by fitting a sum of several decaying curves to every energy bin along the time-dependent spectrum. The decaying time constants and respective signal amplitudes are extracted. This model allows one to disentangle different decaying processes competing within a certain region of the TRPES.

The mathematical model of DAS is a linear system of decay rate equations. The population is represented by linear system of coupled differential equations:

$$\frac{d}{dt}\mathbf{c}(t) = K\mathbf{c}(t) + g(t). \quad (4.2)$$

Here $\mathbf{c}(t)$ is a vector corresponding to each region of the photoelectron spectrum, and

K is the transfer matrix. The entries in K determine the decay rate of each decaying contribution to the spectra with time-constant τ . The diagonal elements of K indicate the total decay of that contribution. Any off-diagonal elements in K represent transition rates between different energy bins, often interpreted as sequential processes. Lastly, $g(t) \propto \exp(-(t - t_0)^2/(2\sigma)^2)$ is the instrument response function, defined as the gaussian temporal cross-correlation between the pump and probe beams. Such a system can be solved analytically, and the solution for each compartment can be formulated as

$$c(\epsilon, t) = g(t) \circledast \sum_{i=1}^n D_i(\epsilon) e^{-t/\tau_i}, \quad (4.3)$$

representing an exponential decay at each binding energy ϵ , convolved with the instrument response (convolution operator denoted by $\circledast$). All time constants, (τ_i) , associated spectra amplitudes $(D_i(\epsilon))$ and parameters in $g(t)$, (cross-correlation width (σ) , and pump-probe time-overlap, (t_0)) are fitting parameters.

The results are shown in fig. 4.5, comparing the raw data in panel A with the fitted DAS in panel B. We see that the fit results are in good agreement, effectively capturing the processes at different timescales and their respective peak heights within the spectrum.

For this procedure we fit three different decay constants. Intuitively, the experimental TRPS appears to have three main contributions. At high binding energies, the features seem to have at least two relatively fast processes, while the lower binding energy region is dominated by a structure with a much longer duration. Inevitably, this selection can be reinforced by theory that shows dynamics for the valence and Rydberg mechanisms manifest into similar ground state products at asymptotic delays but different intermittent decaying signals with very different timescales. Further justification of three-component selection is done by looking at the experimental spectrum with singular value decomposition, as discussed later in 4.2.2.

The different time constants extracted from fitting equation 4.3 are 54(5), 151(15),

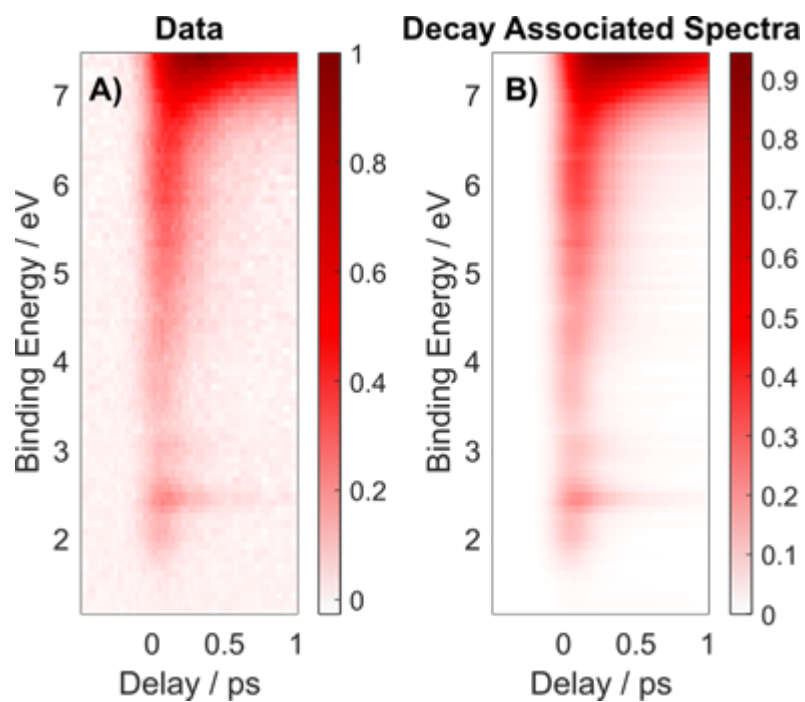


Figure 4.5: A) Background subtracted time-resolved photoelectron spectrum for the excited state region, with dimensions reduced to 70 energy bins. B) Fitting results for decay associated spectra, which is in good agreement with the measurement.

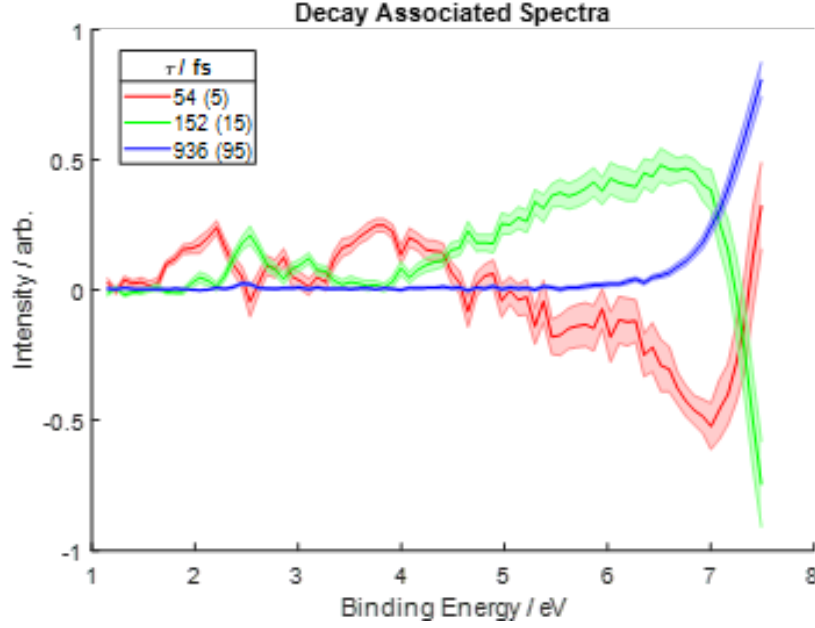


Figure 4.6: . Represented with the coefficients $D_i(\epsilon)$ in equation 4.3 for all the fitted timescales. Positive amplitudes associated with signal decay at the respective timescale, while negative amplitudes indicate enhancement, possibly from sequential processes.

and 935(95) fs. These timescales are of the same order as that of previous measurements of the QC/NBD system and are reminiscent of the timescales from theory.

Figure 4.6 illustrates the decay associated spectra. This representation shows the weight of the signal for the certain decay contributions in each energy compartment (parameters $D_i(\epsilon)$ in eq. 4.3). Positive associated spectra signify decay in that energy bin at the fitted timescale, while negative indicates signal enhancement.

Firstly, the very fast time scale of 54 fs is attributed to the fast relaxation dynamics along the mixed Rydberg-valence $3p_x/V$ states. These associated spectra appear in the expected binding energy region, especially the high positive terms between 1 and 4.5 eV. The negative parts of this associated spectra at lower binding energies above 5 eV could signify the final product formation of hot QC or NBD that occurred via relaxation along the valence states. In comparison to the qualitative timescales observed in the theoretical model of the valence pathway, they are in good agreement. Relaxation along the S1 state

occurs on a timescale of nearly 50 fs with the final ratio of QC/NBD occurring on that timescale as well.

Secondly, the slower timescales, lasting 151 fs, are attributed to deexcitation along the higher-lying Rydberg states. These decaying signals appear in the prominent narrow 3p and 3s peaks at about 2.6 and 3.1 eV, respectively. As expected, contributions from these components are negligible in the region of densely populated valence pathways, especially at the lowest binding energy at 2.0 eV and the intermittent region to the ground state between ~ 3.0 and ~ 4.0 eV. However, near the ground state region above 5 eV, a large positive contribution to the DAS appears. This could be a signature of staggered decay on the S_1 manifold, originating from ballistic wavepackets coming out of the higher lying repulsive surfaces, but bypassing the conical intersection to the ground state on the first pass and remaining on the S_1 state (Figure 3 of the paper) . This process is observed with the decaying feature in S_1 at the bottom of figure 4B in the paper, as the decay initiates at around 250 fs.

Lastly the very slow timescales of 935 fs could signify decay of hot-ground state features as they form dissociative products or change the distribution of vibrational modes at long timescales. The associated spectra that fit to these large timescales are at the highest binding energies above 7 eV. It is this region that is attributed to the hot ground state of QC and NBD. The associated spectra for these slow timescales overlap with the very fast negative associated decay, again a signature of product enhancement. This overlap could signify that these long-lived features correspond to some dynamics in the NBD that are promptly formed via the valence relaxation. The theory shows that both fast valence and slow Rydberg relaxation pathways leads to the long-lived band slightly above the first ionization binding energy. Hence, we can compare the timescales extracted from DAS with those from experiments more sensitive to ground state dynamics, as well as longer timescales for this experiment.

In conclusion, applying DAS fitting to the excited state dynamics provides insight into

the time-dependent signal, enabling qualitative corroboration between the experiment and the theoretical simulations. More importantly, these quantitative timescales can be used to compare different experiments, especially those involving pump wavelength dependences.

Singular Value Decomposition and Error analysis

Processing the raw data for DAS analysis is straightforward and nearly identical to what is shown in the paper. The static PES is subtracted from the time-dependent PES to reveal subtle pump-probe effects that overlay the strong direct ground state ionization background. For further noise and baseline suppression, a threshold is applied, such that any part of the TRPES signal with an absolute enhancement of less than 1% is set to zero. Lastly, the TRPES is down-binned so that the two-dimensional map is comprised of 70 equally spaced energy bins. Down-binning the data this way makes this global analysis tractable, while still maintaining all the features in the raw data.

As with any fitting model, one must carefully select the number of fitting parameters to adequately capture all features of the experimental spectrum while simultaneously avoid overfitting to an unreliable model with too many free parameters. When selecting the number of decaying parameters in the case of the TRPES measurement here, one can intuitively select the number of distinguishing features in the spectrum as a starting point. Again, three features are clear through visual observation, including the broad fast valence decay, the narrow and slow Rydberg decay, and lastly the long-lived feature at high binding energy. The selection of three terms is further reinforced by analyzing the dataset with a generalized decomposition of the data. We perform this operation with singular value decomposition (SVD)¹²⁷. The TRPES data matrix is decomposed into a three-term matrix multiplication:

$$M = U\Sigma V^* \tag{4.4}$$

Here, M is the $m \times n$ TRPES data matrix with m energy bins and n delay points. U and V

are unitary matrices with dimensions $m \times m$ and $n \times n$, respectively. The diagonal matrix Σ contains the singular values of the basis sorted hierarchically. Along the diagonal of Σ , the values are sorted largest to smallest, indicating the significance of the basis vector that is contained in matrix V . A good estimate for the number of the necessary fit parameters is the number of singular values necessary in the basis to unambiguously observe features in the spectra.

Figure 4.7 shows the result of the SVD analysis. The singular values are plotted in the top panel, and it is noteworthy that only three are prominent before plateauing. Upon examining the TRPES matrix with largest contributions (i.e., setting all other terms in Σ to zero except the one denoted and generating the TRPES data matrix via $M = U\Sigma V^*$), we see that they have structure along both axes until the fourth term, where the composite spectra become noisy. Thus, we can confidently assert that it only takes three components to represent the entirety of the TRPES, and consequently claim that three decaying terms may adequately represent the TRPES.

The fitting parameters were extracted by using the least square fitting between the experimental data and the two-dimensional function from eq. 4.3. The optimization was performed by setting wide boundary conditions on all of the fitting parameters and utilizing Matlabs's multistart tool with 200 iterations¹²⁸. To assess the effectiveness of this solver, the optimization routine was applied to twenty different bootstrapped datasets, wherein shots at each delay bin were resampled with replacement prior to shot integrating and pulse energy normalization¹²⁹. The decay constant values and confidence intervals are extracted from the mean and standard deviation of these bootstrapped results, as are the values and errorbars presented in the associated spectra figure. The values and errorbars are all reasonable, and no significant overlap between these values would lead to ambiguity in the assignments anywhere in the fitted spectra. Lastly residuals between the fit and the raw data do not show any structure that would signify improper fitting, as shown in fig. 4.8.

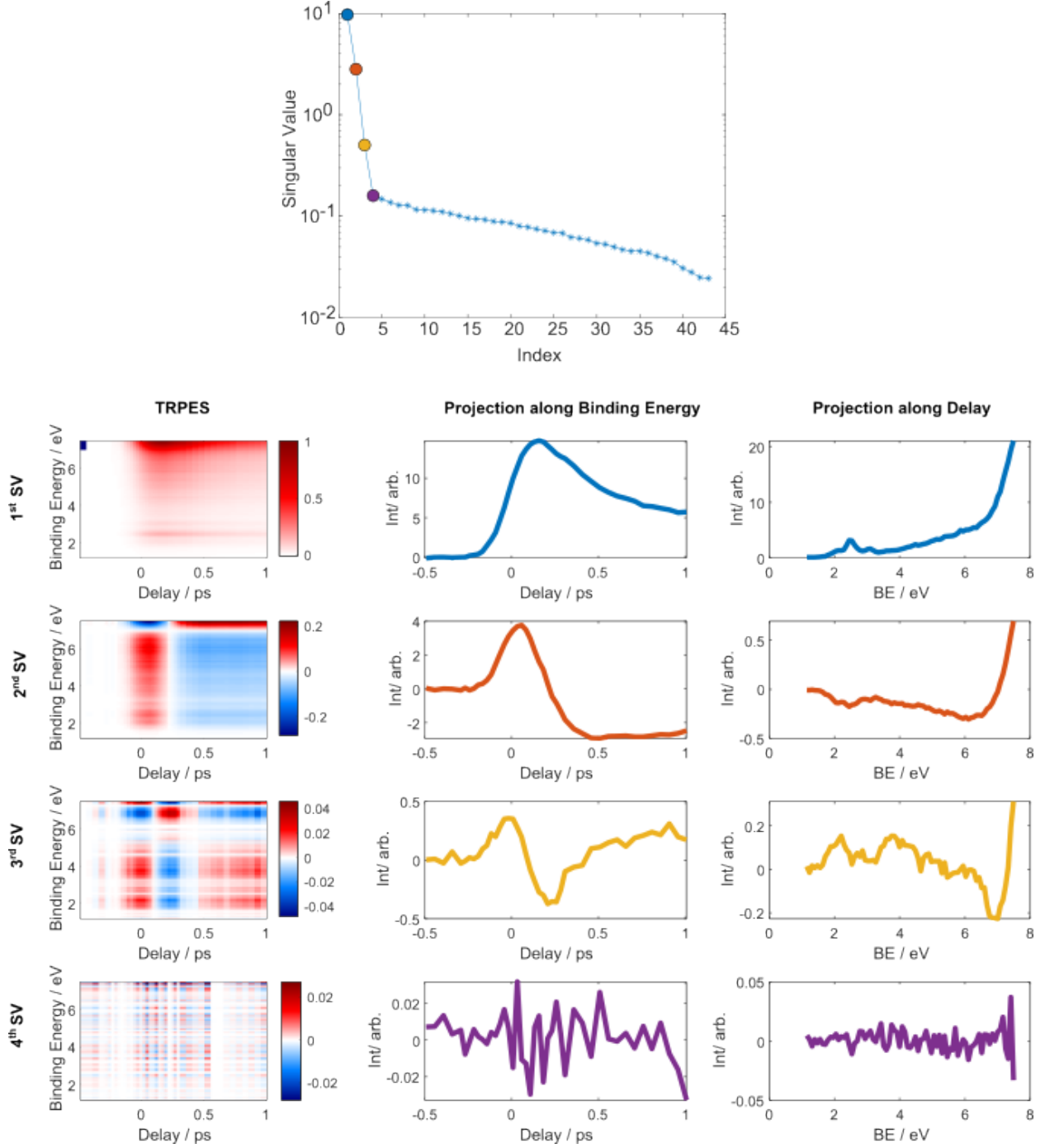


Figure 4.7: Singular value decomposition of spectra. Upper panel: singular values of the 2-dimensional experimental dataset. At indices below the fourth index a distinction between important contributions and noise is clear. Lower panels: the reconstructed dataset keeping only the denoted singular value. For the first, second, and third, singular values (SV) the signals show obvious structure, while the fourth SV is indistinguishable from the noise.

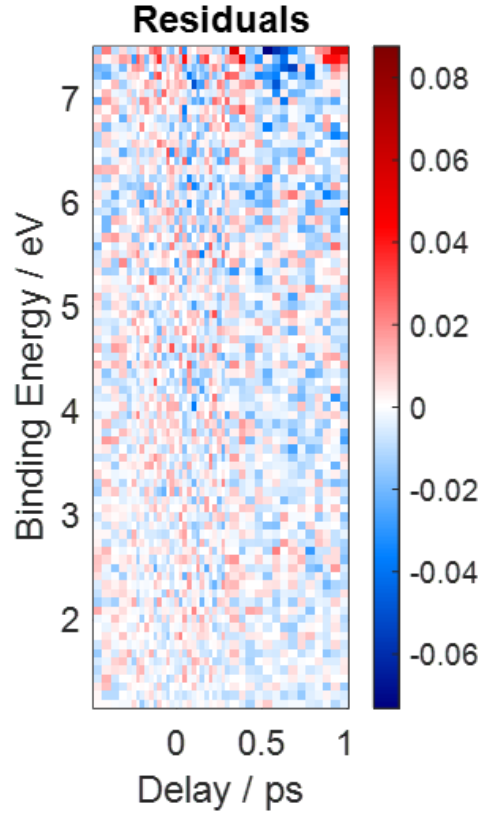


Figure 4.8: *Residuals between the measured spectra and the DAS fitting. The near absence of structure insinuates that the selected model is adequate, and the global parameters reliably represent the processes throughout the excited state signal.*

4.2.3 Ground state dynamics and fragmentation

The above section is focused on the dynamics of photoexcited quadricyclane when probing the relaxation pathway through the higher lying states ($> S_0$) and ionization into the D_0 cationic states. Although this region of the binding energy spectrum can adequately tell us what contributes to the relaxation mechanism, to understand the fate of the photoexcited molecule it is important to look at the spectra of the ground state region and ionization into higher cationic states. Because the FEL photon energy is high enough to probe to the electronic ground-state of the molecule, as well as any excited states, we may explore how the dynamics in the Frank-Condon region can dictate properties upon reaching the ground-state, such as whether the different accessible relaxation pathways all lead to the same ground-state products, and whether those products form on different timescales. In application, it will be these ground state dynamics that will be the main mechanism of interest for molecular photoswitches in the QC-NBD system.

Additionally, it is in this region where TRPES measurements can be used for comparison to different imaging measurements. Especially for the case of coherent x-ray scattering (CXS)²¹ and ultrafast-electron diffraction (UED)²². These methods directly probe changes in nuclear structure, but are comparatively limited in time resolution and, unlike TRPES, cannot disentangle the different electronic states.

In the data presented in this section, nearly all experimental parameters are identical to those in section 4.2.1, except for the applied retarding potential. Here, a reduced retardation of voltage 5 V was used to enhance the transmission of low kinetic energy (the higher binding energy) features. This enables us to observe changes in the lower lying valence orbitals of the QC spectrum. As the sub-eV Rydberg peaks are unimportant for this measurement, the diminished spectral resolution at these lower retardations due to the smaller electron time-of-flight is of minimal concern. For this data, the delay was sampled finely near t_0 up to 1.5 picosecond with equal spacing at each step, while at longer delays up to 600 picoseconds, it was sampled with coarse unequal spacing.

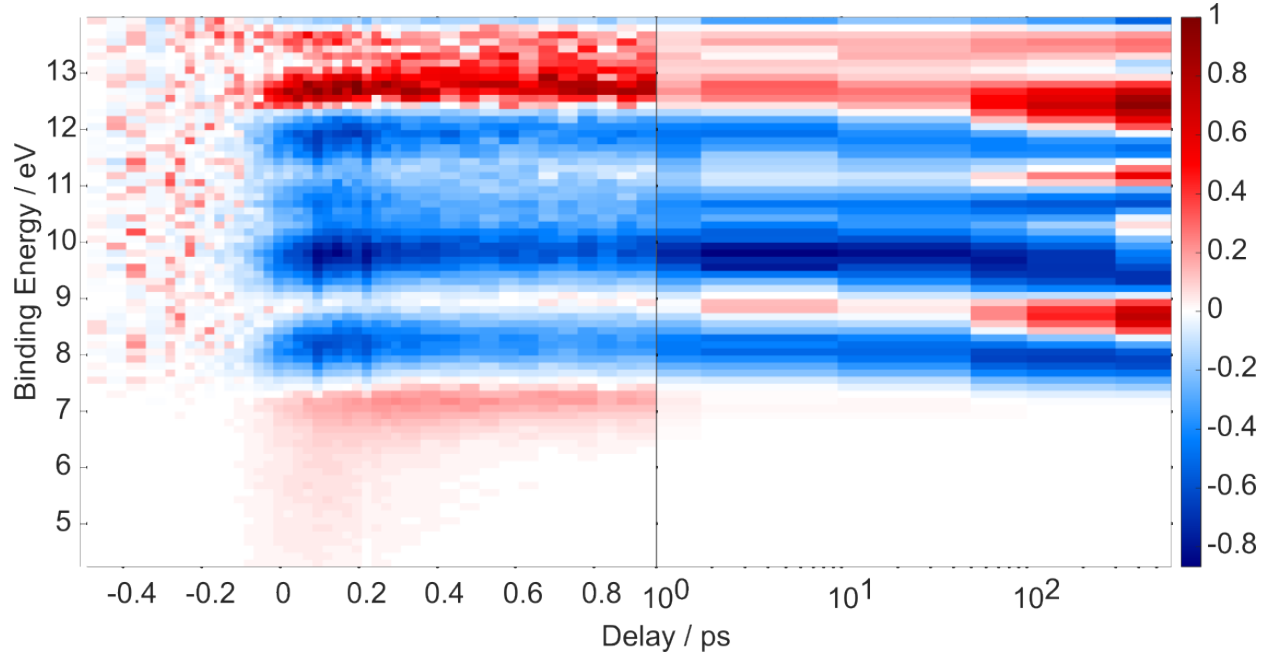


Figure 4.9: *from panel showing the signal from ionization of ground-state D_0 and higher lying cationic states.*

The ground state two-dimensional time-resolved photoelectron spectra is shown in fig. 4.9. The time axis is shown in a combination linear-log scale, to simultaneously show both the fast features at short delay times and the slow variations at long delays. Like fig. 2 in the paper included in section 4.2.1, we observe the fast decay pathway from 4 to 7 eV resulting in the long-lived feature attributed to the ‘hot’ quadricyclane product, and the onset of ground state ionization. Now with the improved transmission we see the extent of the depletion and subsequent dynamics in the ground state.

Figure 4.10 shows the difference spectra at a few single delay points. Near pump-probe overlap we see a strong depletion in the ground state signal, as nearly all spectral components are negative upon excitation. The strongest depletion occurs within the first 200 fs, times associated with the ultrafast relaxation along the S_2 states. Outside of this short time window however, the ground state spectrum shows little variation. The peaks from the ionic states of D_0 , D_1 , and perhaps D_3 , centered around 8, 10 and 12 eV respectively change in neither centroid energy nor width. The heights of these peaks remain similarly

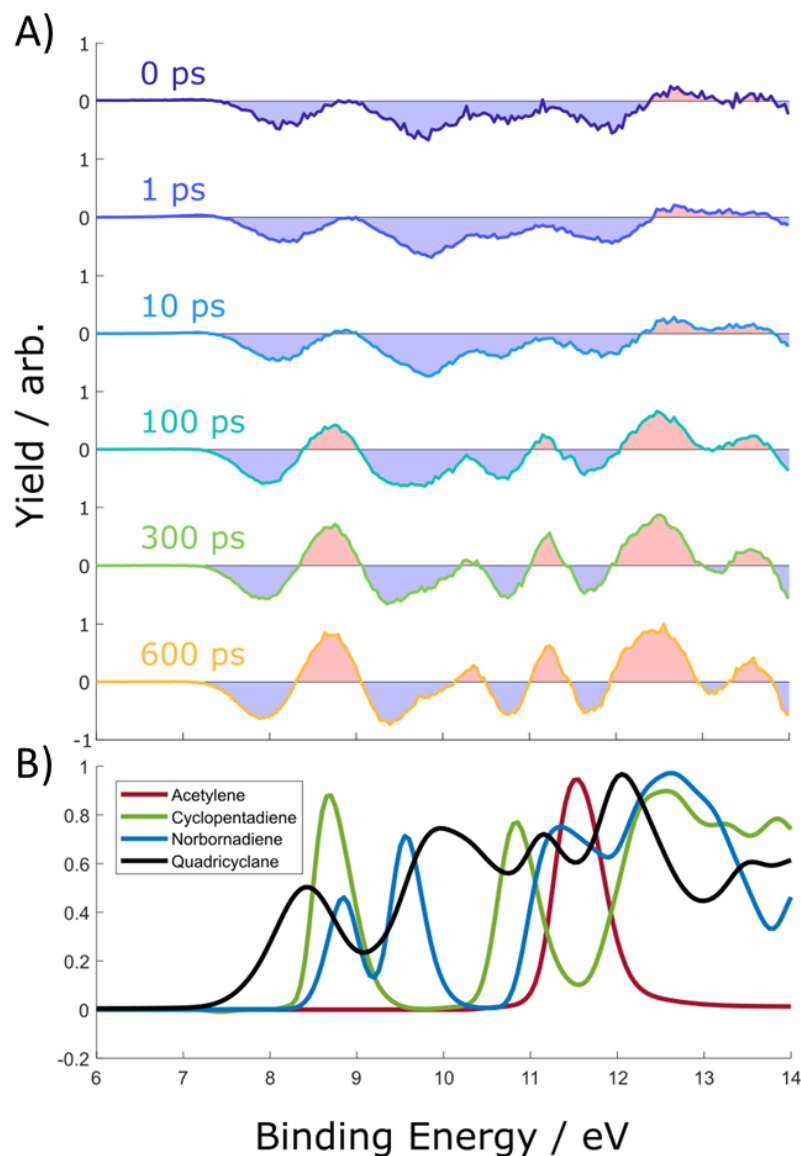


Figure 4.10: Photoelectron spectra for different long-scale pump-probe delays after subtraction of the signal from shots with no UV pulse. A) Spectra are shown on the absolute scale with no additional scaling after being offset for visualization. B) Reference spectra of expected isomers of QC and dissociative photoproducts. See text for references. Delay-dependent photoelectron intensity spectrum of QC at the higher binding energy region from panel showing the signal from ionization of ground-state D_0 and higher lying cationic states.

unchanged beyond 200 fs which may be attributed to a ground-state revival or product formation that plateaus at equally fast timescales, scenarios which are discussed below. However, at large timescales beyond 10 ps, features of the spectrum change significantly. While the depleted negative region intensity remains unvaried, there are notable shifts in the central binding energy of many peaks, and more importantly strong positive contributions form in new regions. It is these features that appear at long delays that could be signatures of product formation of different isomers or fragments, also discussed below. Clearly, the PES is complex and all peaks in the features are intrinsically broad, and further broadening compared to the ‘cold’ ground state spectra may occur from vibrational modes activated via the relaxation processes. These properties make it difficult to truly disentangle all features in the ground state PES.

To extract temporal properties, we look at the time-traces at short and long delays at certain energy bins of interest, particularly those from S_0 depletion and areas of expected product formation. Figure 4.11 shows the signal intensity as a function of delay in a mixed linear-log scale on the horizontal axis. Again, this mixed scale better illustrates different properties of the delay dependence between short and long timescales, with the former remaining unvarying only 100 fs after time-zero, while the latter clearly shows large enhancements growing logarithmically at hundreds of picosecond timescales.

The ground state kinetics can be thought of as a combination of prompt depletion and enhancement that saturates after an infinite time. the former is treated as an instantaneous decrease in signal amplitude (Heaviside step function $\Theta(t - t_0)$), while the latter is a cumulative distribution function of the exponential distribution $f(t) = (1 - \exp(-t/\tau))\Theta(t - t_0)$.

This model is convolved with the instrument response function ($g(t)$, as in eq. 4.3) and can be written analytically as

$$(g \circledast \Theta)(t) = \frac{1}{2}A \exp\left(\frac{\sigma^2 - t\tau + t_0\tau}{\tau^2}\right) \left(1 + \operatorname{erf}\left(\frac{t - 2t_0}{2\sigma} - \frac{\sigma}{\tau}\right)\right) \quad (4.5)$$

$$(g \circledast f)(t) = \frac{1}{2}B \left(1 + \operatorname{erf} \left(\frac{t - 2t_0}{2\sigma} \right) + \exp \left(\frac{\sigma^2 - t\tau + t_0\tau}{\tau^2} \right) \operatorname{erfc} \left(\frac{t - 2t_0}{2\sigma} + \frac{\sigma}{\tau} \right) \right), \quad (4.6)$$

where $\operatorname{erf}(x)$ and $\operatorname{erfc}(x)$ are the Gauss error function and complimentary error function, respectively.

As there may be many different competing product formations in the ground state region, we can model the time-trace in each energy bin as a sum of exponential enhancements (eq. 4.6). In an analogous way to section 4.2.2, we can determine their associated spectra. For values within the first picosecond, the entirety of the dataset was modeled with this “enhancement associated spectra” global fitting scheme to extract two time-constants (using eqs. 4.5 and 4.6).

As shown in section 4.2.2, features in the excited state comprise at least two competing processes that both decay to the ground state. The higher binding energy region for those ground states may comprise final products of those fast excited -state processes. The time constants associated with this transfer to the ground state may have similar associated *enhancement* timescales, τ . This enhanced associated spectroscopy (EAS) is performed in the same way as the DAS. Again, the assumption of two contributions to the fitting model is reinforced by the necessity of two singular values to faithfully reconstruct the difference spectrum in the high binding energy region.

The enhancements for these two time-constants are shown in yellow and blue dashed lines, while the depletion of the signal is shown in the dashed green line. The sum of these three contributions is shown with the solid black line, which adheres to the measured data well.

The optimization routine outlined in section 4.2.2 is slightly modified. The associated spectra for enhancement signals were forced to be positive in value, as negative exponential decay in equation 4.6 would have no physical meaning. Secondly, regularization on the extracted associated spectra was used, including Tikhonov regularization that enforced small

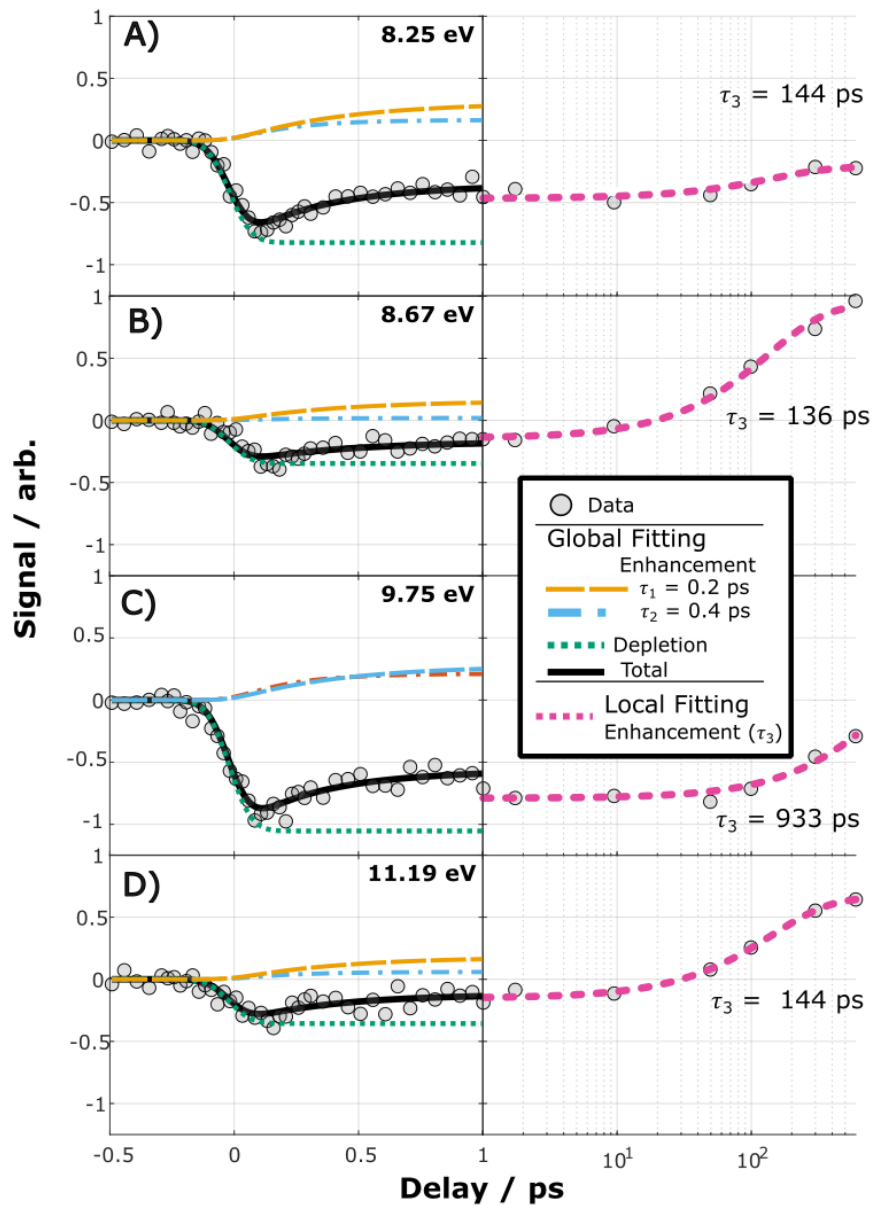


Figure 4.11: Delay-dependent photoelectron yields at various binding energy bins. These traces were selected for ionization to D_0 cationic state (panel A), and expected photoproducts of interest (panels B through D, see text).

values in the associated spectra¹³⁰, such that the constants A and B in eqs. 4.5 and 4.6 were on the same signal height as the actual measured data. Lastly, smoothness of the associated spectra was enforced to avoid non-physical discontinuity in the associated spectra.

The two time constants, extracted from the global fit, show the ground state formation is occurring via two ultrafast processes. Each enhancement time constant has different contributions to the ground state spectra and possible correlation to dynamics that occur in the excited state. First, the faster process has a time constant of 200 fs. The associated spectra of this time constant, shown in yellow in fig. 4.12, are structured with definite peaks, similar in central energy as peaks in the QC ground state, but slightly shifted to lower binding energy. As there were two distinct timescales associated with the higher lying excited states, this shorter enhancement feature could correspond to the final product formation of the valence relaxation pathway. The DAS analysis of the faster contribution in fig. 4.6 showed evidence of this faster valence relaxation being a complex sequential process, with a mixture of decaying (positive) and subsequent relaxation (negative) contributions, the complex mechanism could lead to timescales in the ground state formations being three times longer than the nominal decay rate.

Second, the slower process has a time constant of ~ 400 fs. The associated spectra of this time constant is much less structured in comparison to the one described above, with only one unambiguous peak at 8.25 eV. The associated spectra do not have any features reminiscent of ground state QC. The broadness of the components of this time-constant could be due to several overlapping products forming that are occurring at the longer timescale, which then cannot be disentangled in the associated spectra.

This longer time constant could correlate with the longer kinetics along the Rydberg excited state and S_1 manifolds, which according to the DAS, has a much more complex relaxation pathway with a clear bifurcation in the positive contributions. Again, this complexity could lead to several different but overlapping products with structural or electronic changes that occur even before reaching the ground state, broadening the associated spectra.

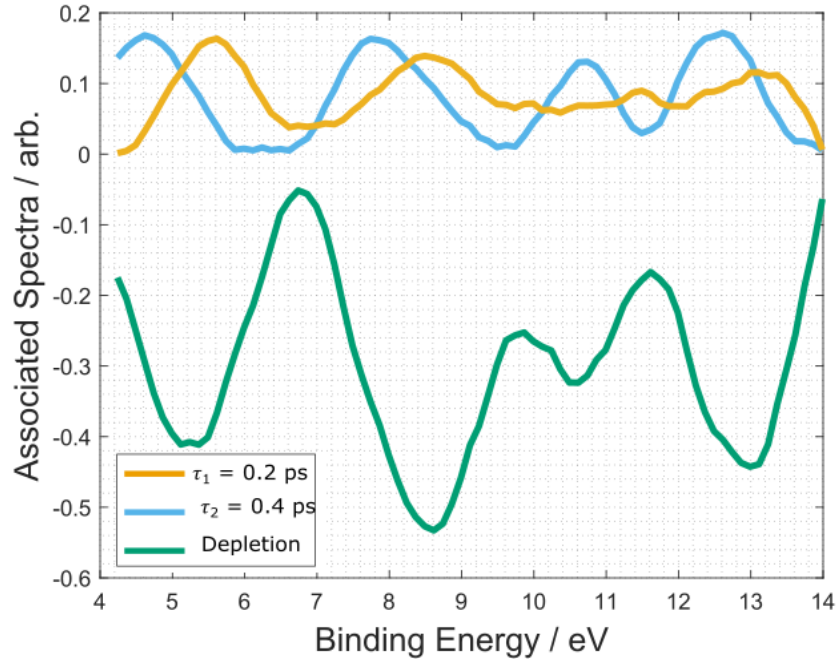


Figure 4.12: *Enhancement associated spectra for the global fitting performed on the dataset for delay times under 1 picosecond. The negative blue line is the amplitudes associated with the decay within each time bin from equation 4.6, while the yellow and orange lines correspond to an enhancement signal.*

Even though the dynamics occurring in the ground state on a short timescale are complex within the first hundreds of femtoseconds and become relatively constant after 500 fs, looking at the spectra at large delays clearly show dynamics occurring, particularly with strong enhancements in certain regions, albeit extremely slowly. At large time delays, the fitting was performed on each respective time-trace to extract the larger time-constants. The results of this fit are shown in the pink dashed line in the right panels in fig. 4.11. Extracting the timescales at these large delays by including them in the global fitting does not work, due to inconsistent sampling between small and large delay points.

The features observed in the TRPES for this binding energy region may offer insights into ultrafast geometric changes that the molecule undergoes. We can compare the results from this data to those obtained from ultrafast techniques better suited to study molecular geometries. Those measurements, combined with previously published photoelectron spectra, serve as a guide for anticipated photoproducts in the ground state.

The QC molecule is complex, and the atomic constituents could rearrange to several configurations. Nevertheless, we expect NBD formation to be prominent, especially from simulations concluding that NBD forms through all excited state relaxation processes nearly 60% of the time. But several other stable isomers could be formed by just breaking one or two carbon-carbon bonds, like the six-membered toluene ring or the seven membered rings or chains.

Dissociation of QC-NB from UV excitation is expected, particularly the removal of an acetylene resulting in the five-membered ring cyclopentadiene (CPD) production. This process was observed using time-resolved mass spectroscopy when studying the relaxation of UV-excited NBD¹⁰⁵. Recently, UED measurements on UV-excited quadricyclane have shown evidence of this dissociation channel, as well as significantly less norbornadiene than expected, constituting only 30% of the final signal¹³¹.

The valence shell photoelectron spectrum of this CPD and acetylene molecules have been studied extensively^{132,133,120,134}, and these spectra are plotted in panel B of fig. 4.10.

Comparing the formation of the vibrationally excited products to these ground state spectra from different ionizing sources is complicated. Different ionizing cross sections would change their relative peak heights. Spectral shifts and broadening due to additional vibrational modes from the photoexcited molecule will introduce further discrepancies.

The most interesting region sits between 8.50 and 8.85 eV where we expect competing signals from NBD and CPD. As fig. 4.11 B shows, this region contains at least two distinct timescales. The fast formation within the ~ 500 fs may signify the NBD formed from both relaxation pathways, but due to limited time resolution and the fact that these peaks would overlap with QC depletion, it cannot be completely separated in the binding energy spectrum. However, with much longer delays we see a prominent peak form at 8.67 eV. Its good agreement with the peak in CPD could show that a dissociation takes place after a very long time in the ground state. Another explanation could be that the highly excited vibrational modes of QC or NBD in the higher lying 'hot' ground state could become more harmonic at long delays, leading to the D_0 photoelectron spectra resembling that of the cold ground state. This may take several hundred picoseconds to manifest.

Formation of NBD remains ambiguous in other regions of the spectrum. There is no obvious enhancement around 9.6 eV for ionizing NBD to its D_1 ionic states. However, it is notable that the negative spectra in this region have significant difference to the ground state QC. Exploring this by examining the enhanced associated spectra for both the ~ 0.2 and ~ 0.4 ps contributions in fig. 4.10 reveals prominent peaks in this region, the former being more prominent at exactly 9.5 eV, very near the ionization to D_1 would be for NBD. These features could insinuate that the hot NBD product could form in this region, which could be shifted to lower binding energies by 1 eV, which would alter the QC depletion spectrum. This phenomenon would also hold for regions above 10 eV and could explain the significant variations in the well-defined peak at 10 eV near overlap that is further altered up to ~ 10 picoseconds.

It is near this region where the second CPD peak near 10.8 eV would contribute, espe-

cially at the larger delays. Indeed, we do see a subtle positive peak appear at 100 ps, and it grows at a comparative rate to its presumed counterpart at 8.67 eV.

Lastly, the evidence of acetylene formation may be most realizable due to its high binding energy. This would avoid competition with strong QC depletion. A prominent peak forms at 11.19 eV, slightly shifting from the expected acetylene peak. This shift could be due to higher vibrational modes formed in acetylene during the dissociation process, or additional contributions from the QC depletion. Again, the timescales associated with this product formation are in good agreement with those from the peak at the “cyclopentadiene” peak at 8.67 eV, providing further evidence that this dissociation channel is ubiquitous at these large delays.

The results in this section show the strength of using XUV FEL sources to probe the dynamics of these molecules using time-resolved photoelectron spectroscopy. The good temporal resolution, high XUV photon energy and adequate fluence enables studying dynamics both in the excited state pathways and probe the inner valence orbitals that were previously unexplored.

There are rich dynamics that occur for several hundred picoseconds in the photoexcited QC system. It is at these timescales where molecular photoswitches for energy applications would be important. As this study was set out to gain insight on the QC to NBD formation upon photoexcitation, it is promising that no unambiguous NBD is observed, providing evidence that the undesired reverse reaction in the MOST system could be avoided under certain excitation schemes. However, as this region of the TRPES is spectrally dense, it is difficult to disentangle all contributing signals. Currently experiments and analysis are ongoing for work that can more directly probe the isomerization nuclear dynamics and will greatly complement the conclusions in this work¹³¹.

4.3 Conclusion and outlook

The results shown in this chapter underscore the strengths of employing XUV-TRPES to probe ultrafast photochemical processes in complex molecular photoswitches. Theory employing non-adiabatic molecular dynamics is in good qualitative agreement with the experiment, and global fitting analysis provides timescales that can be compared to other experiments, including the same experimental scheme probing relaxation of photoexcited norbornadiene, and particularly, different pump-pulse wavelengths. Furthermore, this investigation should be complemented by other experimental approaches more suited to probe molecular geometry. For instance, photoelectron-photoion coincidence or covariance mapping measurements would greatly aid the narrative of photofragmentation at long timescales. Additionally, ultrafast electron diffraction and ultrafast X-ray scattering experiments hold promise for studying molecular reconfiguration at conical intersections. The collaborative team has already performed several of these experiments and their promising results are being analyzed and written at the time of this thesis.

Chapter 5

X-ray multiphoton-induced Coulomb explosion images of cyclic hydrocarbon molecules

In this chapter, we demonstrate that intense X-ray free-electron laser pulses trigger a rapid and nearly complete Coulomb explosion on complex cyclic hydrocarbons. We obtain recoil-frame images that provide signatures of the molecular geometry of homocyclic hydrocarbons prior to the Coulomb explosion process. The results demonstrate the efficacy of Coulomb explosion imaging of molecular targets which have neither site specificity for the x-ray absorption, nor unique markers within the molecule that can uniquely define coordinates of the recoil frame. Employing a simple Coulomb explosion simulation allows for understanding of the complex Newton plots these types of molecules produce.

5.1 Background and motivation

The central theme of this thesis is implementing different XUV and X-ray probing techniques to study ultrafast changes in complex molecules. The previous two chapters contained exam-

ples of time-resolved photoelectron and absorption spectroscopy. Although these methods provide rich information on the changes in the electronic structure and can extract timescales of relaxation pathways, these measurements only indirectly probe reconfigurations of molecular geometry. In those measurements, there was no direct observable corresponding to the nuclear positions within the molecule, nor was there any measurement or observable for the photoions that could provide such information.

In this chapter we will focus on measurements that employ Coulomb explosion imaging to distinguish different complex cyclic hydrocarbon isomers. These molecules have the same chemical formula (C_7H_8) but very different geometries. Imaging the changes in geometries of cyclic hydrocarbons upon UV excitation, a photoisomerization process, has been achieved using time resolved scattering methods such as ultrafast coherent x-ray scattering and electron diffraction^{21,22,135}. Although these scattering techniques can extract the timescales on which these isomerization reactions occur and can provide insight on the products formed, they do have limitations. For example, the signal strength for changes in light atoms is weak due to their small atomic scattering form factors when compared to larger atoms with higher nuclear charge^{136,137,138}. This may omit significant information as many of the electrocyclic ring opening reactions are dictated by rotations that occur at the sites of the molecule where only orientations of hydrogens will unambiguously show the molecular motion^{139,140}. Additionally, the scattering signals of these measurements will only provide information of internal coordinate distances, and information about bond angles cannot be explicitly extracted¹⁴¹. Thus, these scattering methods are still only limited probes of molecular geometry and often rely heavily on simulation and modelling for a more intuitive understanding of the extracted geometry of the photoproducts. These shortcomings show that additional methods are needed for a probe that can provide a more intuitive representation of molecular geometries and their ultrafast changes upon photoexcitation, of which Coulomb explosion is a promising candidate.

Several studies have employed ion momentum imaging to differentiate different isomers.

These studies correlate the momentum of photoions from a molecule to extract molecular geometries. Five-fold coincidence measurements using strong field ionization have been able to differentiate enantiomers, which are different molecules with the same bond connectivity but mirror images of each other^{142,143}. Three-fold coincidence measurements using synchrotron X-ray ionizing radiation were employed to distinguish geometric isomers, where a functional group differs in planar symmetry on either side of a double bond¹⁴⁴. Similar measurements were performed on conformer isomers, sharing a similar structure to the geometric isomers but containing a single bond instead of a double bond, facilitating easier rotation of functional groups¹⁴⁵. The latter two measurements were indirect in that they observed breakup of the functional groups from the carbon-carbon bridge, resulting in molecular ions rather than the atomic constituents. The differentiation between isomers relied on relative angular distributions in the breakup plane that did not provide a true image of the molecule. The reason for this is that the low brilliance of the synchrotron source is unable to drive higher order photon absorption processes, and thus the charge states accessible are limited to the trication. Hence a complete molecular breakup could not be achieved. However, with the application of X-ray free electron lasers, very high charge states can be achieved, ostensibly ionizing all atomic constituents, and having a subsequent complete breakup of the molecule^{1,146}. This enables Coulomb explosion imaging of different atomic sites in the breakup frame in heterocyclic geometric isomers with strong absorption sites.

The Coulomb explosion for three different isomers with the chemical formula C_7H_8 is explored here. This is the same chemical formula as the multicyclic quadricyclane and norbornadiene molecules discussed in chapter 4. However, unlike the subtle geometry differences between those two molecules, the molecules in this chapter vary in cyclic and non-cyclic geometry, the number of carbons in a cyclic group, and the possibility of different conformer geometries. These molecules are shown at the top fig. 5.1 panels A-C. They include toluene, a methyl group attached to a phenol group; cycloheptatriene, a non-planar seven membered ring; and heptadiene, a non-cyclic isomer that can have several conformers. These

molecules provides a good opportunity for development of the Coulomb explosion imaging analysis techniques, as they present some key challenges. The size of these molecules leads to many high energy photoions formed upon breakup, and true coincidence measurements may be infeasible. The lack of planar symmetry in these molecules requires higher-dimensional analysis, as a lot of the ion momenta will be out of the recoil plane. Most importantly, there is no preferential absorption site within the molecule and the lack of unique atoms in the molecules prevents a unique way to define the recoil plane, as there are no unique ‘marker momenta.’

These C_7H_8 isomers are all commercially available and their very different geometries provide a unique opportunity to look at several possible geometries a cyclic molecule could possess during a ring opening reaction with CEI. Aside from the ubiquity of toluene as a fuel additive, motivation to study these isomers specifically is the ring reconfiguration reaction that has been observed in their ionic states. Ionization of toluene induces several molecular rearrangements. One such reaction is hydrogen loss at the methyl site, forming a benzyl radical that still possesses a substituted six-membered ring geometry, followed by the formation of the seven-membered tropylium radical^{147,148,149}. Measurements employing photoion-photoelectron coincidence have determined tropyllium and benzyl form from both toluene and cycloheptatriene with nearly equal abundance, but with different formation energies¹⁵⁰. Recent measurements using linear ion-trap mass spectroscopy coupled to VUV synchrotron radiation also showed tropylium formation from benzylium¹⁵¹. Time-resolved mass spectroscopy measurements observed internal conversion on the the first excited and ground cationic states of toluene occurring within 2 picoseconds¹⁵². However, the exact geometric reconfigurations remain elusive. The imaging methods in this chapter will provide insight to this ring reconfiguration reaction.

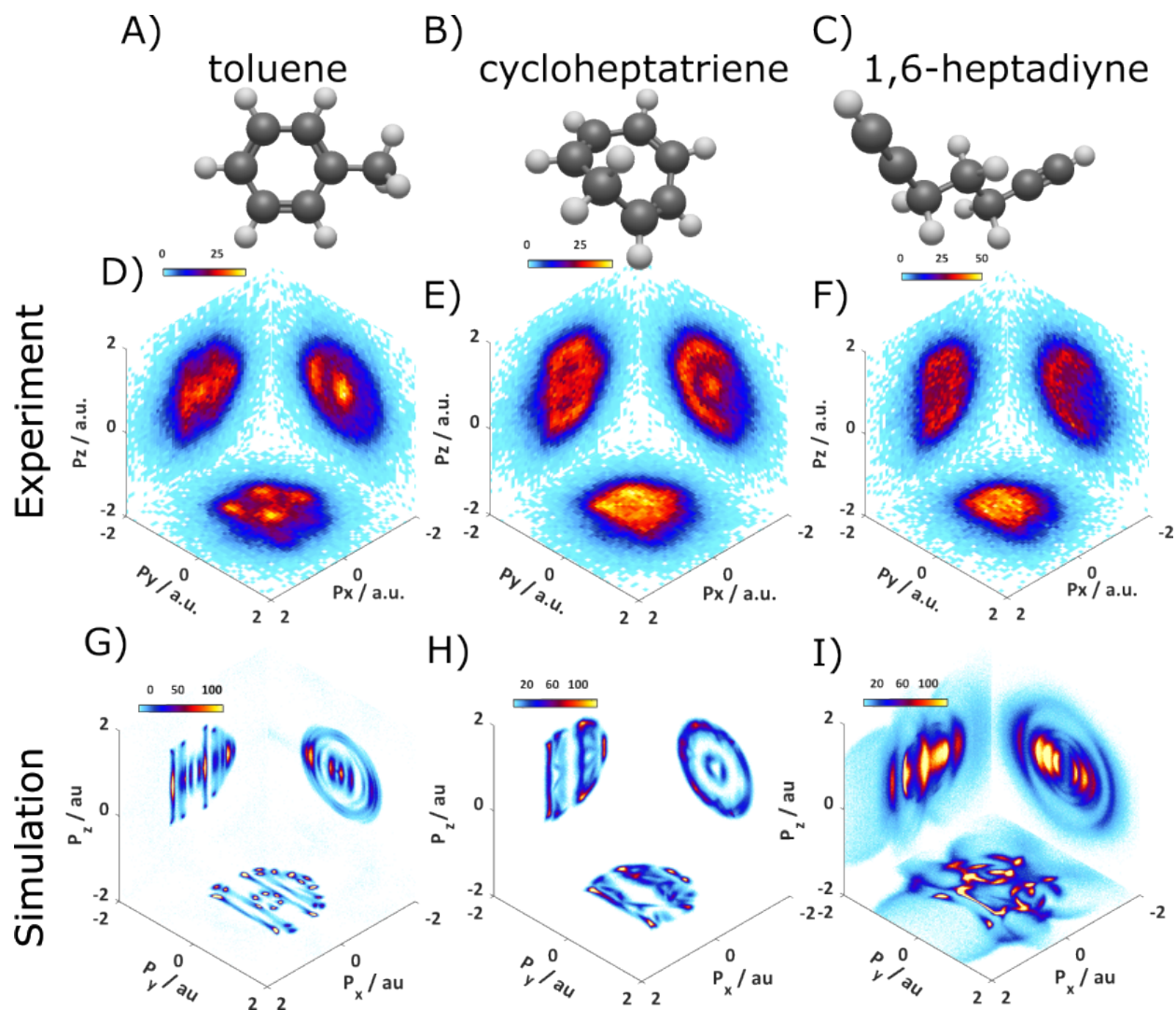


Figure 5.1: Molecular geometries and Newton plots: A) toluene B) cycloheptatriene C) 1,6-heptadiyne. D-F) Experimental Coulomb explosion imaging results represented with three-dimensional Newton plots. G-I) Simulated Newton plots.

5.2 Principles of Coulomb explosion imaging

The principle of Coulomb explosion imaging is that several electrons are removed from a molecule during a prompt ionization reaction, thus populating a highly charged cationic state. The potential energy of such a state is assumed to be nearly Coulombic along some intramolecular separation between atoms and the molecule subsequently breaks apart. So long as there are enough electrons removed, and it was done fast enough that the molecule does not undergo structural rearrangement during the charge-up process, the distribution of asymptotic momenta after dissociation can provide a verification of predicted distributions of molecular geometric configurations^{153,154}.

A schematic of the Coulomb explosion for a diatomic molecule is shown in fig. 5.2, which shows the asymptotic kinetic energy values of the photoproducts. This illustrates that the measured kinetic energy release of the photoions corresponds to the Coulombic potential for the ionic state and asymptotic energies of the ion, and thus the internuclear spacing.

The key to elucidating Coulomb explosion imaging measurements is a prompt ionizing mechanism. Various methods have been employed, including colliding molecular ions with thin foils^{155,156,157}, ion-neutral cross-beam collisions^{158,159,160}, electron impact¹⁶¹, and, as is the case for this thesis, different ionizing radiation. The latter offers several advantages, including the ability to conduct pump-probe measurements with femtosecond resolution, and in the case of X-ray radiation, providing site-selectivity to an atom within the molecule. On a single-shot basis, all photoions are measured with a time and position sensitive detector for extracting their three-dimensional momentum. Here, spectrometer techniques like those discussed in section 3.2.2 are employed. With appropriate characterization of molecular and light beam interactions, the center-of-mass frame can be defined for the molecular breakup.

Within this center-of-mass reference frame, energy sharing between ions and their relative emission angles encode information about the molecular geometry upon breakup. One representation is the recoil frame, as shown in fig. 5.4 with a *Newton plot* for breakup of a triatomic molecule. This plot shows the coordinate transformation that orients the system

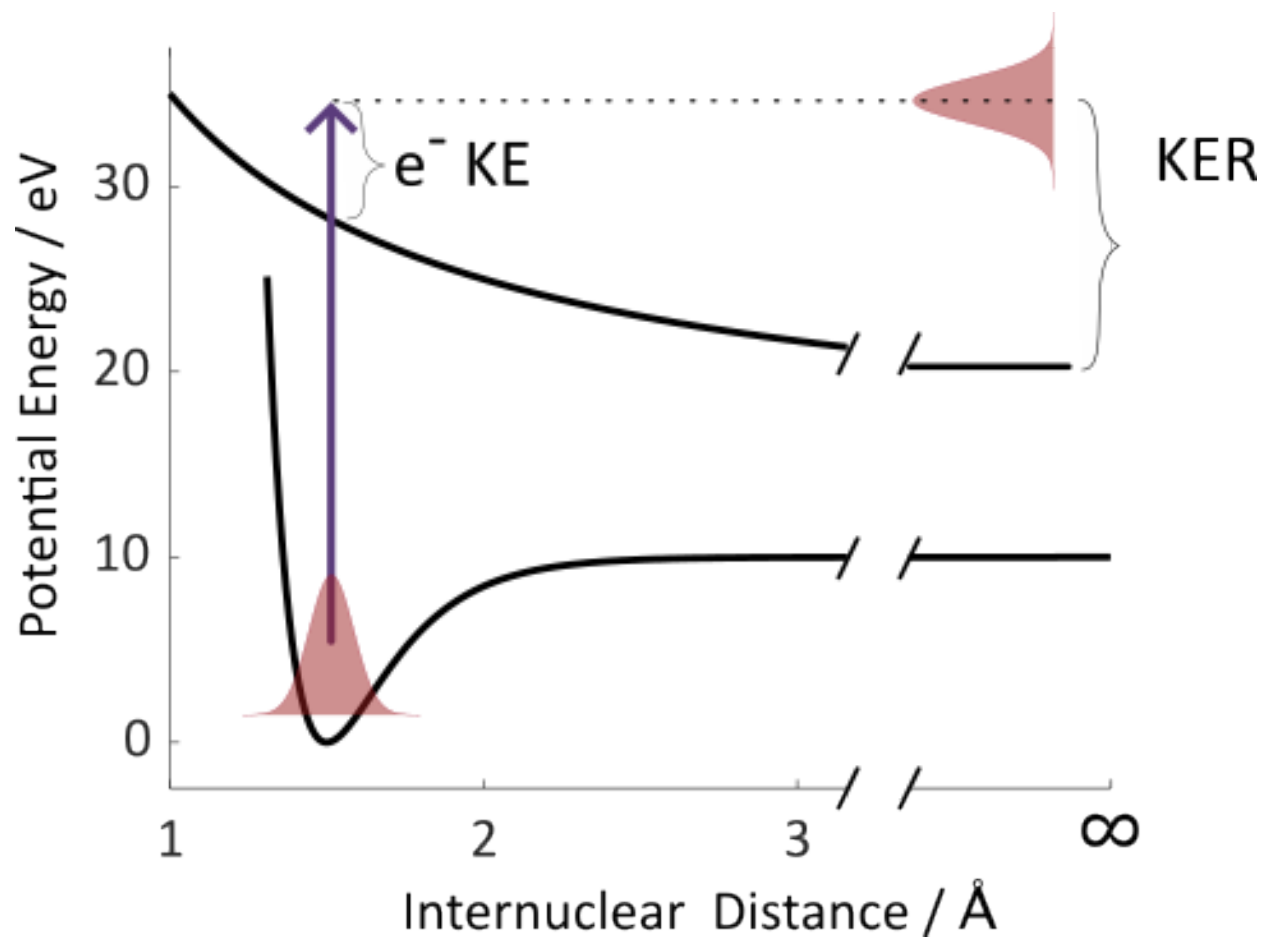


Figure 5.2: *Coulomb explosion process of a diatomic system. The measured kinetic energy release (KER) can be mapped to the internuclear distance.*

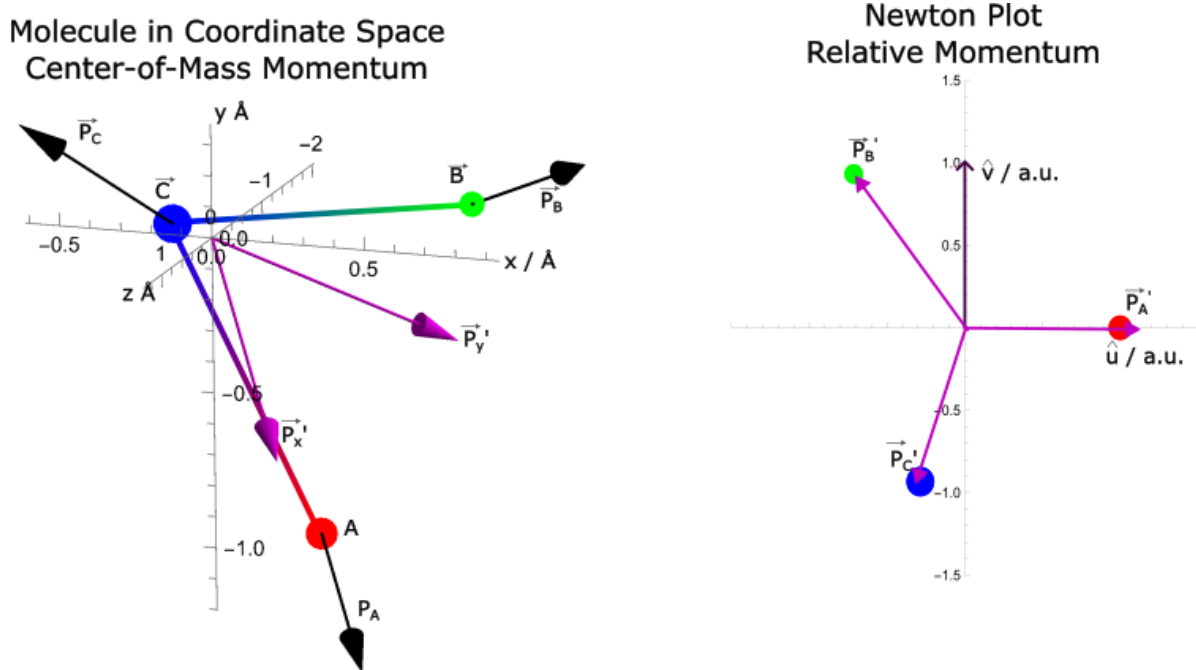


Figure 5.3: Schematic for orienting the momenta of three-body breakup to a recoil frame, which is visually represented with the plot for a triatomic system. Position coordinates in the left panel are in angstroms, while the momenta in the right panel are normalized to the reference ion momenta P'_A , as is the convention for this chapter

such that the emission of the ions can be represented with respect to a plane. The plane is defined by the momentum vectors of two of the particles measured. One particle's momenta (e.g., P_A) is rotated onto the x-axis (denoted by unit vector $\hat{u}$). A second particle's momenta (e.g., P_B) will have a component perpendicular to this new axis. It is this perpendicular component that will define the y-axis in this recoil frame (denoted by unit vector $\hat{v}$). These two momenta are called the reference momenta, and the momenta distribution of all other particles (e.g., P_C) are plotted in their recoil plane. It is this recoil plane that can be thought of as the molecular frame that provides a possible visualization of the molecular geometry. For molecules with more atoms than a triatomic, the other ions that are not used as references can be plotted in the same way as vector P'_C , including out of the plane defined by $\hat{u}$ and $\hat{v}$. But as we discuss in this thesis, significant complications arise if the molecule has no unique ways to define the recoil plane.

5.3 Coulomb explosion imaging of C_7H_8 isomers using X-ray FELs

In this section we discuss the results and analysis of an experiment performing Coulomb explosion imaging on different geometric isomers with formula C_7H_8 .

5.3.1 Experimental results

This experiment was performed at the European X-ray Free-Electron Laser at the Small Quantum Systems endstation with the cold target reaction microscope discussed in section 3.2.2. The molecules were introduced into the chamber as a dilute gas jet through supersonic expansion. X-rays from the FEL were incident on the molecular beam with a photon energy of 1.5 keV focused to a micron in diameter with approximately 2 mJ pulse energy. The pulses were estimated to have a 15 fs pulse duration. The effective repetition rate of the FEL was 600 Hz. The breakup events are selected with three-particle coincidences. All three detected particles were selected to be C^{2+} ($m/q = +6$ atomic units). This is the highest charged channel with meaningful statistics. It needs to be noted that as we only detect three of up to fifteen different atomic constituents, the rest of the true charge state of the molecule in each shot is unknown and all observables presented here are integrated over several different possible charge configurations greater than or equal to total charge $Q = +6$ atomic units, however, as will be shown in the following section, selecting ionization events where three C^{2+} are produced leads to a high likelihood that nearly all other atomic constituents are also at least singly charged, such that the ambiguity of the explosion is less severe than one might initially suspect. Selecting coincidence events where all particles are identical complicates the analysis, and data processing corrects for possible artefacts, as discussed in section 5.4.

Figure 5.1 panels D-F show the experimental three-dimensional Newton plots for the three different isomers. These Newton plots are presented such that the two reference

momenta define the xy -plane, and projections on the yz - and zx - plane can be presented on the respective perpendicular axes. There are differences in these Newton plots for the three isomers, as detailed below, although they do not resemble the molecular geometry as clearly as the work of Boll, et al¹.

The breakup of the planar-molecule toluene in panel D exhibits the most structure. Most of the molecular breakup is contained in the central xy -plane, and we see islands of high momenta concentric to a large central blob near the center of the of the Newton plot.

The cycloheptatriene breakup in panel E has fewer distinguishing features. Some subtle features are present in the Newton plot. However, they primarily lie in the yz - and zx - planes, which are perpendicular to the breakup plane of the reference ions. Three horizontal stripes in the xz -plane at about $z = \{-1, 0, 1\}$ are distinct. These features become concentrated when projected onto yz -plane, with an obvious concentrated circle at the center.

The heptadiyne breakup is the least intuitive, as the breakup of this molecule shows no features in the experimental Newton plot. The Newton plot is a single indistinguishable blob in all three planes. The expected geometry of this molecule is non-cyclic and planar, so some other underlying property of this molecule may cause such uninformative Newton plots, and we will explore this later in the chapter.

5.3.2 Simulation results

Interpreting these Newton plots is greatly aided by performing a simple Coulomb explosion simulation for these molecules. For these simulations, every atomic constituent of the molecule is promptly set in motion via their Coulomb interaction. The equations of motion for these interacting particles are solved numerically and the asymptotic momenta are extracted. These momenta are then used to build the recoil frame Newton plots in the same manner as the experimental data. To provide some semblance of the inherent momentum distribution that would be expected in the experiment, we use several thousand geometries from the zero-point energy vibrations of the molecule simulated using TD-DFT

calculations¹⁶².

Again, the Newton plots are defined with specific reference ions whose momenta define the xy -plane. Obviously in the simulation, we can specifically select these reference ions from atomic sites in the molecule. However, the features in the Newton plots vary significantly depending on the reference ions selected. We exemplify this phenomenon using toluene. Figure 5.4 shows several Newton plots, projected onto the xy -recoil plane with different reference ions. Like the experimental data, the reference momenta are not shown, but the remaining five carbon momenta are plotted. For toluene, some of these Newton plots are very reminiscent of the six membered ring geometry, with varying degrees of asymmetry in the xy -plane (highlighted with a green frame). In others, structure is lost, either as the projected momentum distributions appear as stripes in the Newton plot spanning the y -axis (highlighted with a yellow frame) or become so diffuse that discretization of the momenta is unobserved (highlighted with a red frame).

Although it is trivial to specify the recoil-frame reference ions in the simulation and look at the Newton plots individually, this is not a straightforward procedure in the experiment, as the mass-to-charge ratio is identical for all detected ions. Thus, for unambiguous sorting for the molecular frame, more information is needed than just the m/q of the ion. The experimental molecular frame is a composite of all possible reference orientations, wherein every carbon site will define the reference axis with equal probability. Including this in the simulation by superimposing all the recoil frames significantly obfuscates the simulated Newton plots, and they are reminiscent of the experiment, as shown in panels D,E and F in fig. 5.1.

For example, the simulated Coulomb explosion plots for toluene in panel D of fig. 5.1 still contain the signatures of a ring geometry, with a low momenta site centered around a larger ring, like the green highlighted plots in fig. 5.4. However, with all reference combinations superimposed, we see that these features become multimodal, and significant out-of-plane contributions appear.

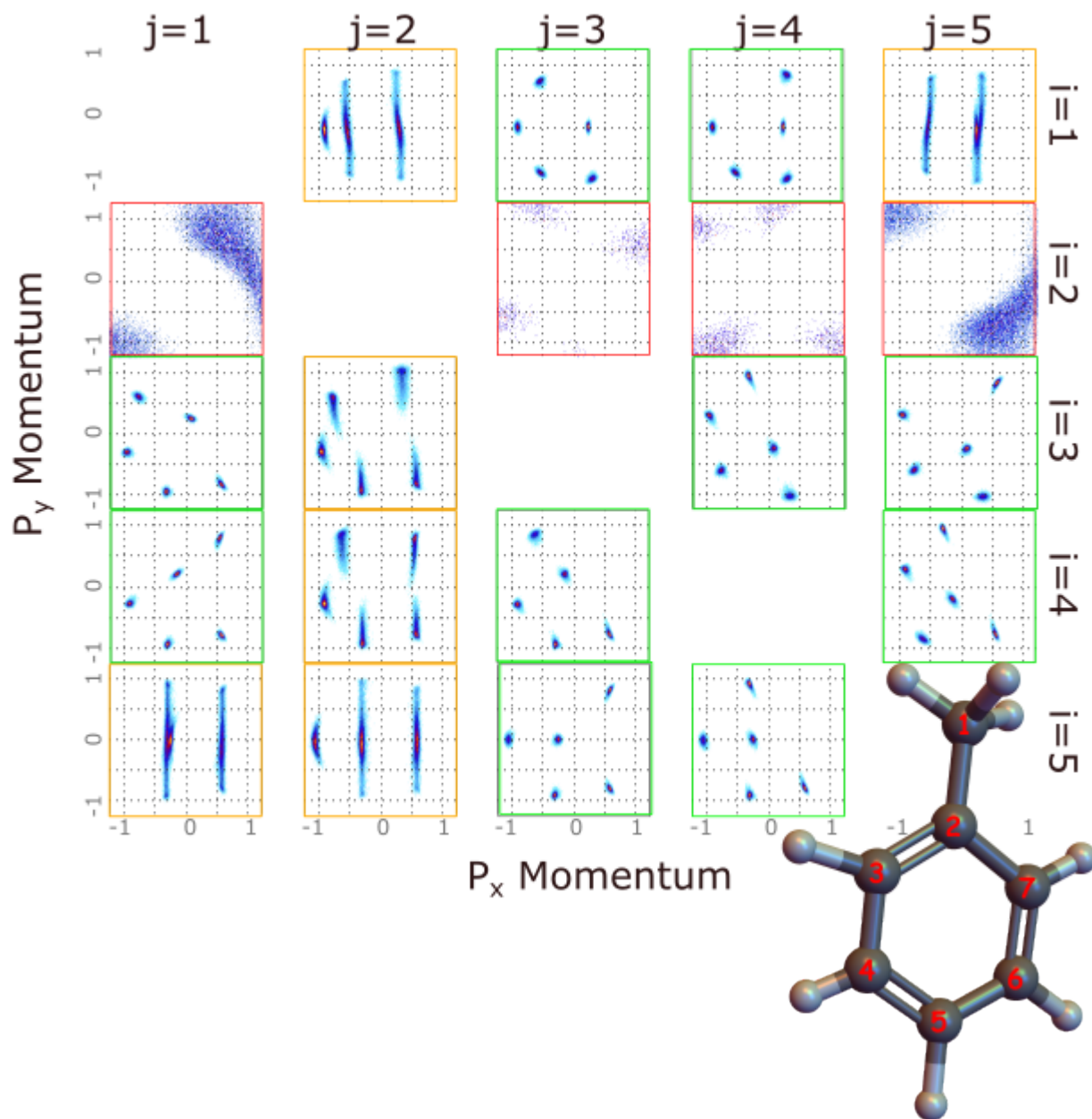


Figure 5.4: *Newton plots for Coulomb explosion simulations of toluene iterating through all combinations of reference ions. Each column corresponds to the carbon site whose momenta defines the x-axis. The rows signify the carbon site whose momentum vector has a perpendicular component to the new x-axis, and thus defines the y-axis.*

The simulation for cycloheptatriene panel E of fig. 5.1 reveals a similar horizontal oblong shape in the yz -plane. Similarly, the sparser center band is revealed when projected onto the zx -plane. On the yz -plane a series of concentric rings appear with an intense center point observed in the experiment.

The non-cyclic molecule heptadiyne simulated image has no semblance of the experimental image, a discrepancy we will elaborate on in the next section. In the simulation, it contains minimal out of plan distribution compared to its cyclic counterparts. Unlike the seven-membered ring, it contains great symmetry on all three planes.

5.3.3 Discussion

We now discuss the results of the Coulomb explosion analysis, with particular emphasis on identifying any key features of the molecular geometry from the experimental Newton plots guided by the simulations. Additionally, any other methods of sorting coincidence data for further extrapolation will be discussed.

Toluene

Toluene, as shown in fig. 5.1 panel A, is a substituted hydrocarbon with a methyl group attached to a phenol ring. It has a symmetry axis defined as the plane on which the methyl and the substituted carbon lie, as shown in fig. 5.5. With this symmetry, we expect significant symmetry in the Coulomb explosion pattern. We will see that the noted axis of symmetry plays an important role in defining the reference recoil frame in an intuitive way.

Figure 5.1 panels D and G compare the results between experimental and simulated toluene, wherein there is no discrimination of the reference ions to build the recoil frame. As stated above, there are similar features between the two. The most prominent feature in the experimental Newton plot is the single central spot near the origin of the xy -plane. This feature also manifests in the simulation, however, it is composed of six individual points centered around $x \approx 0.5$ au and sparse in the center. The next prominent features are diffuse

‘islands’ that surround the central point in the xy -plane. Although these features appear asymmetric about the x - and z -axes, it is important to note that a lot of this asymmetry is due to building these Newton plots without the reference ions being plotted, neither in the experiment nor the simulation. Similar features that form an outer ring appear in the simulation, however, in a similar manner to the inner ‘ring’ they display several multimodal properties. The multimodal properties in the simulation are due to the inclusion of all possible recoil frame combinations. When carbon sites that sit on the same line as the methyl group are excluded as the reference ions (carbon-2 and -5), the resulting Newton plot shows an intuitive picture of the breakup and the corresponding geometry, particularly the high energy emission of the carbons on the phenyl ring and an obstructed low energy emission of the carbon-2. This impedance is due to opposing forces on the ion from its neighbors^{163,164} (i.e., from carbon-1 at the methyl site and all other carbons in the phenyl ring). The resulting Newton plots are nearly circularly symmetric when the methyl group carbon momenta defines this x -axis ($i = 1$), and all other carbon momenta off the axis of symmetry define the y -axis (can be any carbon in the group $j = \{3, 4, 6, 7\}$). When the case is reversed (horizontal reference can be any carbon number in the group $i = \{3, 4, 6, 7\}$ and $j = 1$), the circular symmetry in the Newton plot breaks down.

Referring back to superimposed features in fig. 5.1 D, the xy -plane also contains elongated horizontal features, seemingly connecting the ‘islands’ on each side of the x -axis. These features occur in simulation when the x -axis is defined with the momentum of the methyl site carbon ($i = 1$), and the other reference is one of the carbons sitting along the molecule’s axis of symmetry ($j = \{2, 5\}$). In this case, these reference ions are emitted nearly back to back, and the reference ion j will have practically no perpendicular component to that of the ion i .

This case of $i = 1$ and $j = \{2, 5\}$ (and conversely $i = \{5\}$ and $j = 1$) leads to the xy -plane being ill-defined, as the reference momentum vectors are nearly parallel or anti-parallel. The breakup frame for using these reference ions then projects onto the planes

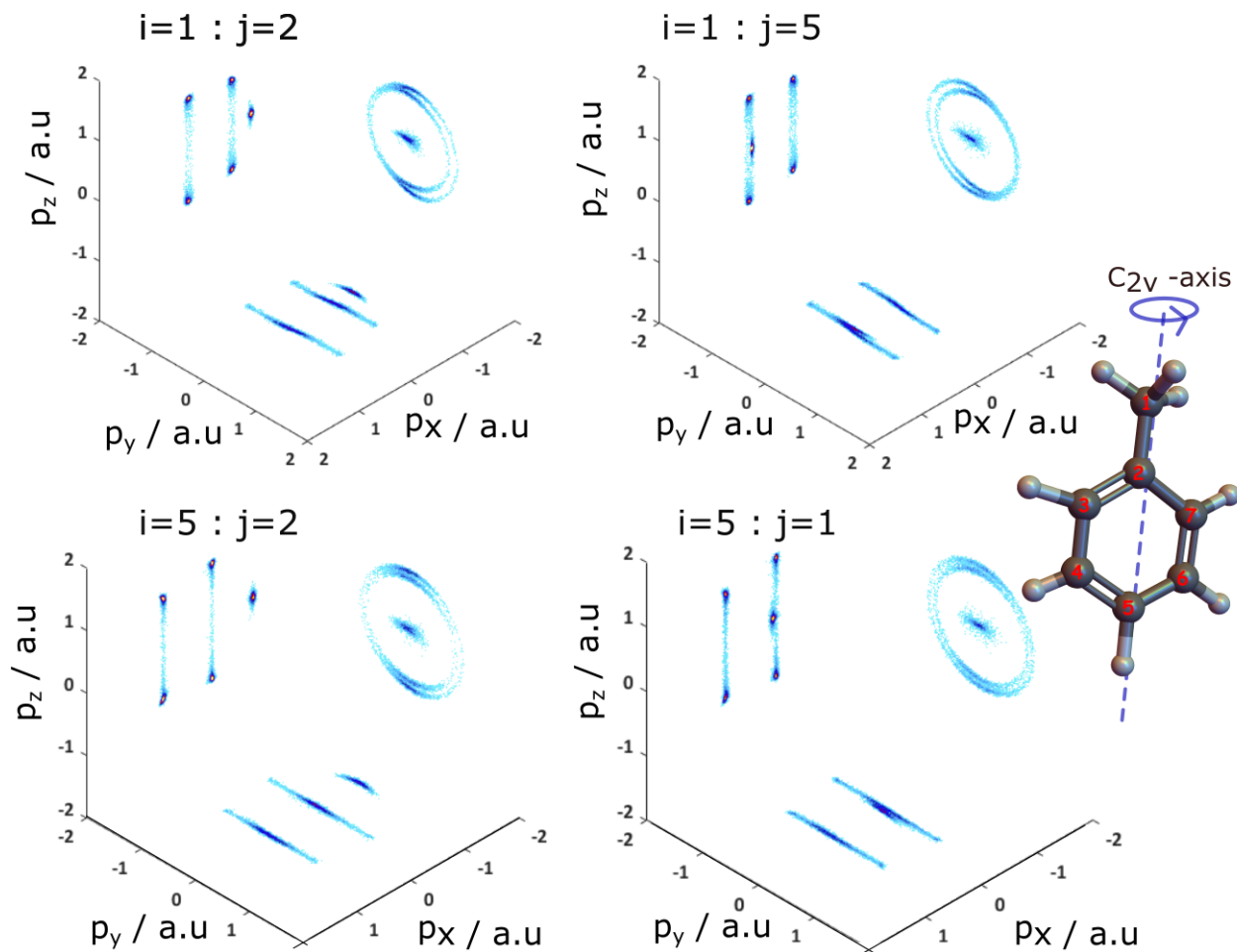


Figure 5.5: *Three-dimensional Newton plots for Coulomb explosion simulations of toluene where the reference ions are defined by carbon sites that are on the axis of symmetry of the molecule.*

perpendicular to the xy -plane, and a lot of non-planar features manifest, unlike the previous scenarios. Here, the planar properties of the molecule make it such that the breakup plane occurs perpendicular to the reference plane, and several of the features seen in the above scenario then manifest in the xz -plane, as shown in fig. 5.5.

The last feature of note for toluene is a diffused structureless feature that is nearly uniform over the entire xy -plane, obvious in both the simulation and the experiment. This occurs when the reference ion defining the x -axis is the obstructed carbon-2. Here, there is no preferential direction for this obstructed ion momentum. These recoil frames are often

defined with normalization to the ion defining the x-axis. So, when the amplitude of the horizontal reference ion momentum is very small compared to the momentum amplitude of the others, the normalization scaling of all plotted ions diverges and a representation of the momentum distribution of the other ions falls out of the plotted range in which all other reference ion combinations are better defined.

As all these simulations show, the Coulomb explosion of these molecules is an indirect image of the molecular geometry as there is no unique markers to define the recoil frame and the Newton plot of all reference combinations become superimposed in experimental analysis. Due to the symmetry of toluene, some features in the Newton plot are reminiscent of the molecular geometry, particularly the low energy feature corresponding to the impeded motion of carbon-2, but all other features become more difficult to resolve and map to the molecular geometry.

However, one advantage of Coulomb explosion measurements is that there are several correlation metrics that encode information on how the molecule has broken apart and what was detected within a shot, and this can be particularly useful for interpreting properties of the reference momenta. Events can be filtered where the reference ions meet certain criteria in their correlations when preparing the final Newton plot. Particularly, these metrics may enable reduction of the combinations that comprise the final Newton plot and provide a better resolved Coulomb explosion image.

Obviously, this would be trivial if one or two of the measured ions were a unique atomic species, but that not being the case for these hydrocarbons, we can instead be energy selective on the reference ions (e.g. removing the low kinetic energy ranges to remove references being defined by obstructed breakup of carbon-2), and relative angle of the reference ions (e.g., assuring that the reference ions are not defined by ions that are emitted back-to-back, which would the xy -plane ill-defined and map the Coulomb explosion image out of plane, as shown in simulation in fig. 5.5).

This routine is exemplified in fig. 5.6. Panel A shows the measured angles between the

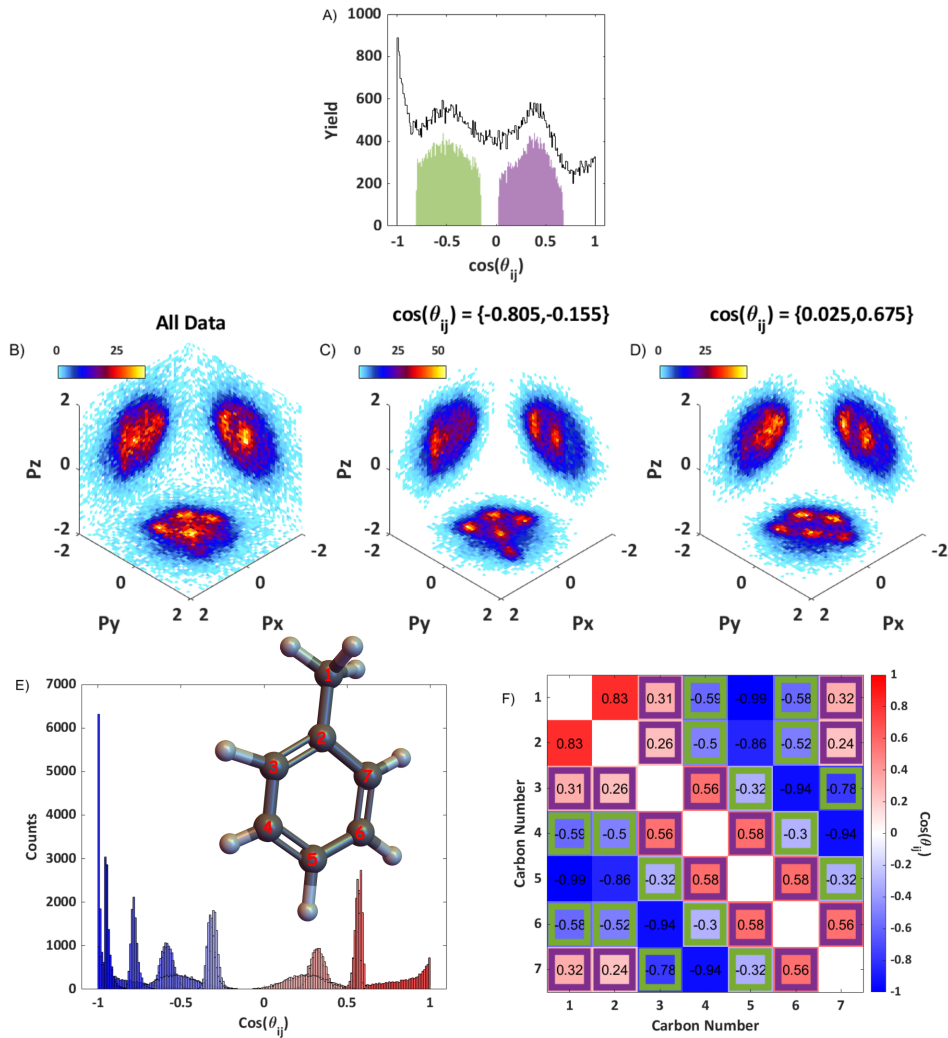


Figure 5.6: Data filtering to site select ions to define reference frame in Newton plots. A) Distribution of angles between ions i and j that will define the recoil frame. B) Newton plot with no filtering. C and D) Newton plot with filtering on angular distribution range in panel A. Panel B is identical to panel 1D in fig. 5.1, with several events randomly removed to have similar statistics in panels C and D for better comparison. E) Distribution of angles in the simulation. F) Matrix that shows the average $\cos(\theta_{ij})$ in the simulated datasets. Color coding is used to aid in the pairings for panel F. Darker blue colors correspond to $\cos(\theta_{ij})$ values closer to -1 (left side of the plot in panel E), darker reds correspond to values closer to $+1$ (right side of panel E). Green and purple squares correspond to reference combinations selected in experiment.

momenta of two randomly selected ions that are used to define the reference ions (these ions are randomly selected, as they have identical mass-to-charge ratios, see section 5.4 for data preparation). The spectrum for angular correlation between any two ions (black line histogram) has four distinct features, including two peaks at $\cos(\theta_{ij}) = \pm 1$, and two broad peaks near $\cos(\theta_{ij}) = -0.5$ and 0.4 . Panel B includes the Newton plot of this data with no filtering, so it is comprising all reference combinations. However, as demonstrated with the simulations, it is intuitive to build the Newton plots if reference momenta are not parallel or anti-parallel. Thus, we can select events that fall within a certain range of the angular distribution in panel A and look at the corresponding Newton plot from those shots. Panels C and D of fig. 5.6 provide examples of this filtering. These Newton plots show events in which the reference ions emit $\cos(\theta_{ij}) \in \{-0.805, 0.155\}$ (green shaded histogram) and $\cos(\theta_{ij}) \in \{0.025, 0.675\}$ (purple shaded histogram), respectively. Additionally, we impose that these reference ions have a kinetic energy larger than 1 a.u. (~ 27 eV), because if the low energy ions are used as references, the breakup plane is obfuscated and diffuse, as discussed above with the simulation. With this filtering, the Newton plots become more clear. We have greatly reduced the number of reference combinations in the Newton plot, selected breakup patterns in which the reference momenta are separated by every other carbon (panel C) or their nearest neighbors (panel D). This interpretation is justified with the absence of the peak on the positive and negative side of the x-axis respectively. It would be in these empty spaces where the reference ion j would be appear, but this reference ion is not plotted for demonstration of the filtering method. We can conclude that by filtering on correlation metrics for the reference ions, we can significantly reduce the contributions in the Newton plot images from all possible combinations.

Again, interpretation of this filtering routine is aided based on the simulation. Panel E in fig. 5.6 shows the simulated angular distribution for all ion pairs superimposed on the same plot. This simulation shows much finer structure compared to the measurement, as we are limited by the experimental angular resolution and multiple competing processes that may

occur in the experiment that are unaccounted for in the simulation. However, the simulation shows a similar trend as the experiment, particularly the large peaks corresponding to parallel and anti-parallel emissions near $\cos(\theta_{ij}) = \pm 1$. Also, a grouping of peaks appears near $\cos(\theta_{ij}) \approx \pm 0.6$ that resembles the two peaks in the experimental data. To best represent which of the pairs corresponds to which peak in the angular distribution, a 7x7 grid is presented in panel F, which provides a color coding for the average emission angle of the ions (also the average $\cos(\theta_{ij})$ is denoted in each block). Looking at these average values for the simulated data provides insight into which reference ions and corresponding recoil frame remain when selecting the data to build Newton plots in panels C and D. Those that we expect to fall in the range $\cos(\theta_{ij}) \in \{-0.805, -0.155\}$ are denoted with a green border. These combinations include not only $\{i = 1, j = 4\}$ and $\{i = 1, j = 6\}$, where the methyl site defines the x -axis, but also $\{i = 3, j = 5\}$ and $\{i = 5, j = 7\}$. The latter two combinations support the assertion that the references that make up the Newton plot in panel C are ions that are spaced two-apart in the phenyl ring. Reference ions whose angles fall in the range of $\cos(\theta_{ij}) \in \{0.025, 0.675\}$ are denoted with purple borders in panel F. These include not only $\{i = 1, j = 3\}$ and $\{i = 1, j = 7\}$, but also $\{i = 3, j = 4\}$, $\{i = 4, j = 5\}$, $\{i = 5, j = 6\}$, and $\{i = 6, j = 7\}$. Again, these simulations show that this range in the angular distributions is built with references that are site selected such that they are neighbors in the phenyl ring.

Cycloheptatriene

Cycloheptatriene (CHT), as shown in fig. 5.1 panel B, is a seven-membered cyclic-hydrocarbon with no substitutions, but contains a methylene site (CH_2) in the ring. Unlike toluene, it is non-planar, with a *chair* conformation because the methylene site and the two opposing carbons sit out of the plane made by the middle carbons 2,4,6, and 7, as denoted in fig. 5.7. But like toluene, it has C_{2v} symmetry, with the symmetry axis at through the methylene site and the double bond that sits at its opposite side of the ring. With this molecular sym-

metry, we expect similar symmetry in the Coulomb explosion pattern. However, because of the non-planar properties of the molecule, the momentum distributions of the recoiling ions has a lot of contribution outside of the ‘*molecular plane*’. This significantly complicates mapping the Newton plot to any molecular geometry.

The results of Coulomb exploded CHT are shown in panels D and G of fig. 5.1. These Newton plots are generated in an identical manner as for toluene in both the experimental and simulated plots. Comparing the Newton plots between CHT and toluene, the structures of CHT are much more complex. The momentum distribution in the xy -plane is abstruse, unlike the case for flat molecules where it is clearly resembles the molecular geometry. This is evident in the simulation, as the xy -plane is comprised of scattered non-symmetric features while the experimental polot is homogenous and unstructured, likely due to inadequate resolution. However, the yz - and xz - planes contain symmetric structures in both experiment and simulation. We will elaborate on the source of these features in the simulation and explain the experimental data by comparing it to toluene’s well understood ion energy and angular spectra.

There are two distinguishing features in the simulation for CHT. In the yz -plane, distinct vertical bands are present while the xz -plane has two concentric circles as shown in panels H in fig. 5.1. The features extending out of the xy -plane are likely due to the non-planar properties of this molecule. To understand the source of these features, we again begin by discussing the several composite recoil frames that build these Newton plots. Again, to best distinguish the possible pairings of the reference ion momenta, we filter the angular distribution between them. This is more relevant for this non-planar cyclic ring than it is for toluene, as the planar properties of the latter molecule consistently manifest as an intuitive picture in the Newton plots xy -plane regardless of the reference combinations, except for parallel or anti-parallel references. The simulated relative angle distribution for all reference combinations is shown in fig. 5.7 A.

Three features are observed in the relative angle spectra. Firstly, the large peak near

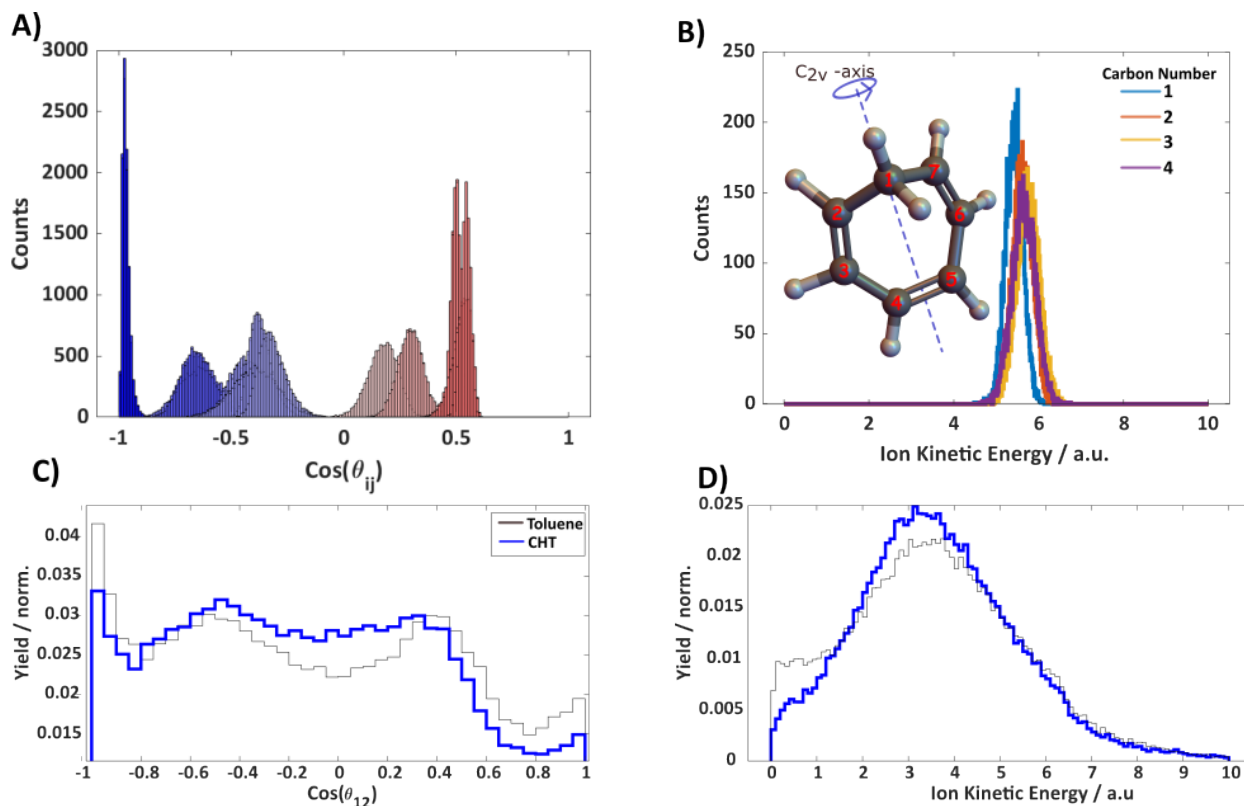


Figure 5.7: Angle and energy distribution for Coulomb exploded cycloheptatriene. A) Simulated emission angle between references that define the recoil frame. B) Simulated kinetic energy for four carbon sites. C) Experimental emission angle for cycloheptatriene and toluene. D) Experimental kinetic energies.

$\cos(\theta_{ij}) = -1$ is due to references emitting anti-parallel from opposite sides of the ring. Secondly, emission of ions from neighboring carbon (e.g., $i = 2$ and $j = 3$) sites correspond to peaks near $\cos(\theta_{ij}) \approx 0.5$. Lastly, alternating carbon sites (e.g., $i = 2$ and $j = 4$) correspond to peaks near $\cos(\theta_{ij}) \approx -0.6$. This general trend of emission from neighboring and alternating carbons sites has a similar motif to the six-membered ring in toluene. For the seven-membered cycloheptatriene, there is no peak corresponding to parallel emission (i.e., $\cos(\theta_{ij}) = +1$), and the near anti-parallel peak does not occur from carbon sites that lie on any axis of symmetry.

Additionally, it is important to note the expected kinetic energy distribution of the carbon ions from cycloheptatriene. As shown with the simulation in fig. 5.7 panel B, nearly all

carbon ions have equal kinetic energy (only 1 through 4 are shown, as the planar symmetry of the molecule makes 5 through 7 identical to 2 through 4). Unlike toluene that had low energy contributions to the spectra signifying the obstructed breakup at the substituted carbon, no such obstructed breakup is expected in CHT. Thus, there are no complications with defining reference momenta from such obstructed ions that cause an ill-defined relative recoil momentum. In toluene this phenomenon leads to significant out-of-plane properties and normalization artefacts. We see no diffuse background from those artefacts in fig. 5.1 H, and out-of-plane properties are due to the non-planar geometry of the molecule.

We now elaborate on some of the features observed in the CHT Newton plot, as shown in fig. 5.8, based on observations for the reference ion metrics. The most obvious feature of interest is the concentric circles in the xz -plane. This is reminiscent of the concentric circles of the toluene xy -plane that is due to obstructed breakup. However, as noted above, there is no expected obstructed breakup in the CHT, and all carbon ion kinetic energies are expected to be similar. Rather, it is observed that these concentric circles are a property of plotting different carbon site momenta with different reference ions. Specifically, the concentric circles occur for all reference ions, so long as carbon-1 (the out of plane methylene site), does not contribute. It occurs for all ion references $i = \{2, 4, 6, 7\}$ and all combinations of j . Two examples are shown in panels A and B of fig. 5.8. The inner circle is created by the carbon site opposite of reference $i \neq 1$, and it has small distribution in the z -direction. This inner circle occurs when combining all possible j -reference carbons. Looking at the projections on the other planes, these momenta site-localize in the xy - and xz - planes at $x = -1$ and are confined to the y -direction at $z = 0$, respectively. If carbon-1 contributes to the Newton plot, it lands on the larger outer circle because it sits outside of the plane of the other carbon atoms. Examples for $i = 1$ are shown in fig. 5.8 C showing that no inner circle appears. Likewise, no inner circle appears for $i = 3$ whose opposing carbon-6 lands on the outer circle, as shown in fig. 5.8 E.

The outer circle is the projection of all other carbon sites with respect to the references,

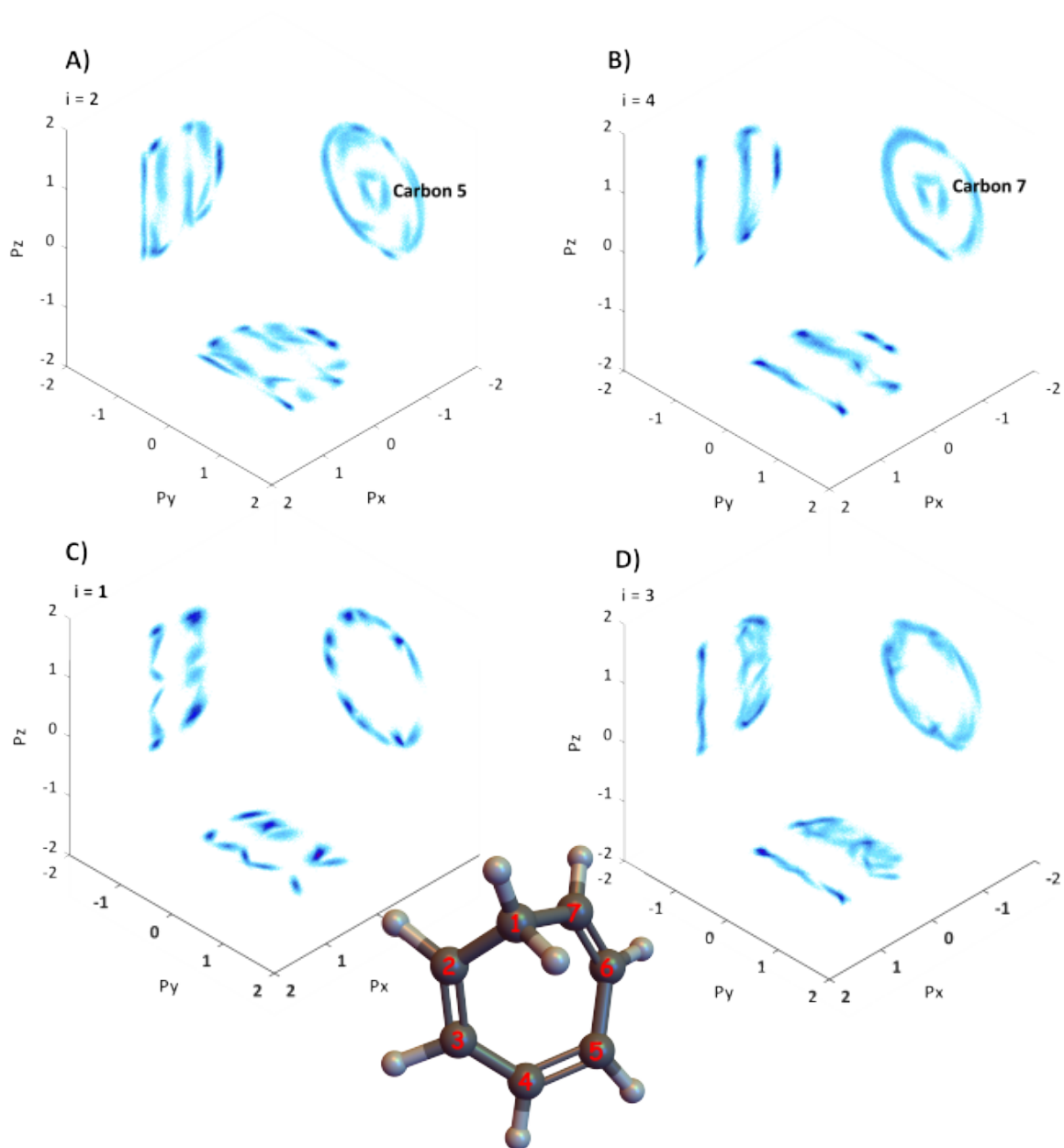


Figure 5.8: Three-dimensional Newton plots for Coulomb explosion simulations of cycloheptatriene for individual reference ions i , which define the x -axis of the recoil frame. All possible permutations of reference ion j , which define the y -axis are included in each plot.

except for those sitting opposite on the ring as discussed above. These carbon sites are not confined to the xy -plane in the respective recoil frames. For projections in the other directions, this ring appears as horizontal and vertical stripes in the xy - and xz -plane. Noteworthy is the large out of plane distribution in the xz -plane for all reference iterations. In the case of reference ion carbon-1, we see a narrow, localized symmetric band near $z = 0$ in the xz -plane shown in fig. 5.8 C. This feature corresponds to the momentum of the carbon site opposite of the reference ion j .

The conclusions drawn from the analysis of the simulation elucidate the experimental results, especially for the goal of being site specific in selecting the reference momenta for the recoil frame in the experiment. Several features in the experimental data agree with the simulated Newton plots. Aside from the unstructured blob observed in the xy -plane of the experiment, the structure in the yz -plane contains the same concentric rings observed in simulation, and the xz -plane is much less distinct, but includes the key features observed in the simulation. Particularly the three horizontal bands at $z = -1, 0, +1$ that occur when the recoil frame is built with carbon site $i = 1$ as the x -axis reference.

We can perform data reduction operations with a metric that correlates the reference ions to enable site specification in the recoil frame, similar to operations on the toluene data by using reference ions with certain energies and relative emission angles. The experimental relative angle distribution is shown in fig. 5.7 C, with the toluene distribution underlaid for direct comparison. The spectra contains the general features observed in the simulation, including back-to-back emission of the ions, and emission from the nearest and reciprocating neighbors, $\cos(\theta_{ij}) = [-1, +0.5, -0.6]$, respectively. These signatures of recoil within the ring are similar to those observed for the fragmentation of the phenol ring in toluene. But for the CHT, the angular distribution shows comparatively smaller signatures of parallel and anti-parallel emission (the non-negligible peak at $\cos(\theta_{ij}) \approx +1$, which would signify parallel emission, could be from other non-uniform charge up processes unaccounted for in simulation).

Of additional note is the single peak in the ion kinetic energy distribution, centered around 3.4 a.u. for the experimental data, as shown in fig. 5.7 D. In the CHT kinetic energy spectrum, there is no low energy shoulder, as observed for toluene that was a signature of the obstructed breakup for the carbon at the methyl substitution site. The simulation overestimates the kinetic energy of the ions significantly compared to the theory, where the spectra peak at ~ 5.5 and ~ 3.5 in the simulated and experiment, respectively. Again, this could be due to several processes in the experiment that are unaccounted for in simulation, particularly if the charge up process is prolonged or several of the carbon ions that are undetected are only singly ionized. Regardless, the simulations show qualitative agreement for the normalized momentum correlation spectra, a phenomenon seen in kinematically complete Coulomb explosion measurements with strong-field ionization¹⁶⁵, providing evidence that any unaccounted processes in the simulation would not necessarily discredit the usefulness of using the simulation as a guide in mapping molecular geometry. With the noted angle and energy distributions of the reference ions, we can perform data filtering in the same way as we did with toluene. For toluene, the reduction of the reference contributions to the Newton plots by selecting specific relative angles was straightforward, as that angle spectrum could distinguish parallel and anti-parallel references, as well as provide signatures of relative positions of carbons in the phenol ring. For the case of CHT, only the latter will be relevant as there are no parallel or antiparallel reference emissions.

We filter the Newton plots with three selections of expected reference combinations, that correspond to the three peaks in the relative angle distributions: back-to-back emissions for $\cos(\theta_{ij}) \in \{-1.00, 0.83\}$, nearest neighbors for $\cos(\theta_{ij}) \in \{0.10, 0.65\}$, and alternating carbon sites for $\cos(\theta_{ij}) \in \{-0.83, -0.30\}$. To validate any conclusions for the plotted measured ions, we perform the same filtering on the simulated data, where identifying the exact carbon site is trivial.

The experimental results of filtering using the angular distributions are shown in fig. 5.9 panels A through D. Differences for each region of $\cos(\theta_{ij})$ are subtle. Nevertheless, they

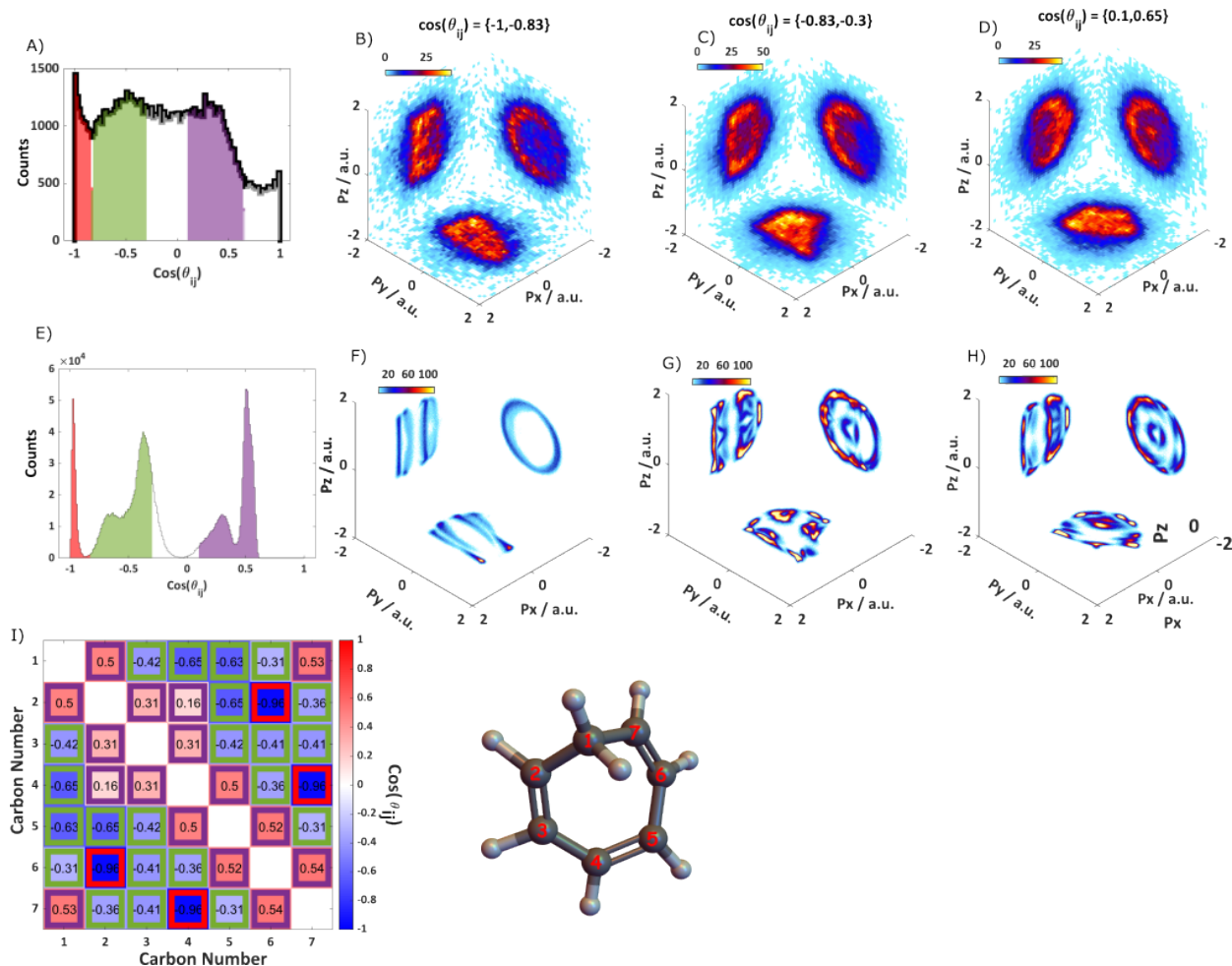


Figure 5.9: Data filtering to site select ions to define reference frame for cycloheptatriene. Panels A through D are experimental results. Panels E through H are simulated results. Panel I: Matrix that shows the average $\cos(\theta_{ij})$ in the simulated datasets. Color coding is used to aid in the pairings for panel A in fig. 5.7. This matrix acts as a guide for which gating region corresponds to which reference ions define the Newton plot.

reveal information about the reduction of permutations that are included in the Newton plots. For the first case of back-to-back emission of the references (fig. 5.9 B) the xz -plane is comprised of a single near vertical stripe centered around $p_x \approx 0.5$ a.u. and extends to $p_x \approx 0$ a.u. In the yz -plane the outer circle becomes dominant compared to the faint inner circle. Panel 5.9 C contains data for the relative angle distribution associated with alternating carbons in the ring. Here we see the inner ring grow in the yz -plane, while in the xz -plane the momentum distribution becomes broader in x -direction with the signature three-horizontal features. The features for nearest neighbor references, as shown in fig. 5.9 D, are similar, with the inner ring becoming even more apparent and the p_x momentum distribution shifting towards $p_x - 1$ a.u.

Applying these same gates to the simulated data, and identifying the fingerprints of the carbon sites, in a similar manner to that of fig. 5.8, helps validate the observations in the experiment. These parsed simulated datasets are shown in fig. 5.9 panels E-H, and are in good qualitative agreement with the experimental data. For the case of back-to-back emission shown in fig. 5.9 F, not only is the outer ring isolated, but dispersed horizontal lines in the xy - and xz -planes appear. As discussed above, these dispersive features are prevalent because the near anti-parallel emission of the reference momenta make the recoil plane ill-defined. Two prominent peaks in the xy -plane near $p_x, p_y = [+1, +1]$ and $[-1, +1]$ a.u. appear due to the two ions between the references being confined along the $p_y = +1$ line.

The case for second nearest neighbors contains richer structure in the Newton plot as shown in fig. 5.9 G, including non-symmetric patterns in the xy -plane. The concentric rings appear in the yz -plane as well, with higher intensity on the outer ring. The three horizontal features in the xz -plane appear in the experimental plot as well, with higher intensity on the outer lying lines near $p_z \approx \pm 1$ a.u. The events for references comprised of nearest neighbors have similar Newton plots to those of second nearest neighbors, as shown in panel 5.9 H. However, the vertical feature in the xz -plane shifts to more negative values in comparison to fig. 5.9 G. Additionally, the middle band near $p_z = 0$ is more prominent.

Although the above discussion illustrates that selecting events based on the relative angular distribution of the reference ions yields different Newton plots for this non-planar ring molecule, the differences are subtle and interpretation for site selectivity is difficult. Ideally, we would reduce the dimensionality further, which would more readily reveal differences in the breakup patterns depending on the selected reference. In essence, with the near uniform kinetic energy for all seven carbon fragments in both experiment and simulation, the Newton plot is nearly radially symmetric for all permutations, as the radius of the momentum in this recoil frame encodes the ion kinetic energy.

We instead look at the recoil frame in spherical coordinates, rather than cartesian coordinates like in the Newton plots. In the case of uniform radial distribution, we can represent the data with azimuthal (ϕ) and elevation (θ) angular spectra.

For the case of references defined by second nearest neighbors, as in panel C of fig. 5.10, a prominent peak appears at $\phi \approx 3\pi/8$ in both experiment and simulation. This peak corresponds to the emission of the carbon located between the two references (i.e., if $i=3$ and $j=5$, then it is carbon 4). Its elevation angle distribution spans the whole range $\cos(\theta) \in \{-1, 1\}$ because it is asymmetric between permutation of those two references (i.e., it lands below the plane for $i=3$, and $j=5$, but lands above the plane when they are flipped). An additional broad structure is observed near $\phi \approx -5\pi/8$. The simulation shows that it is comprises nearly three features with complex structure. These features originate from the ions that sit on the other side of the ring relative to the two reference ions.

For the nearest neighbors shown in fig. 5.10 D, the signature peak near $\phi \approx 3\pi/8$ is absent for both experiment and simulation. Rather, an extended feature near $\phi \approx \pi/4$ is present. Similar to the prominent peak at $\phi \approx 3\pi/8$ for panels C discussed above, this peak corresponds to the carbon site that sits nearest to the references, specifically one site above reference i (e.g., if $i = 3$ and $j = 4$, this is a signature of emission for carbon site 5). This trend of identifying ions originating from carbons atoms near the references is broken for carbon-1. This carbon sits far out of the molecules plane. It does not appear for any of its

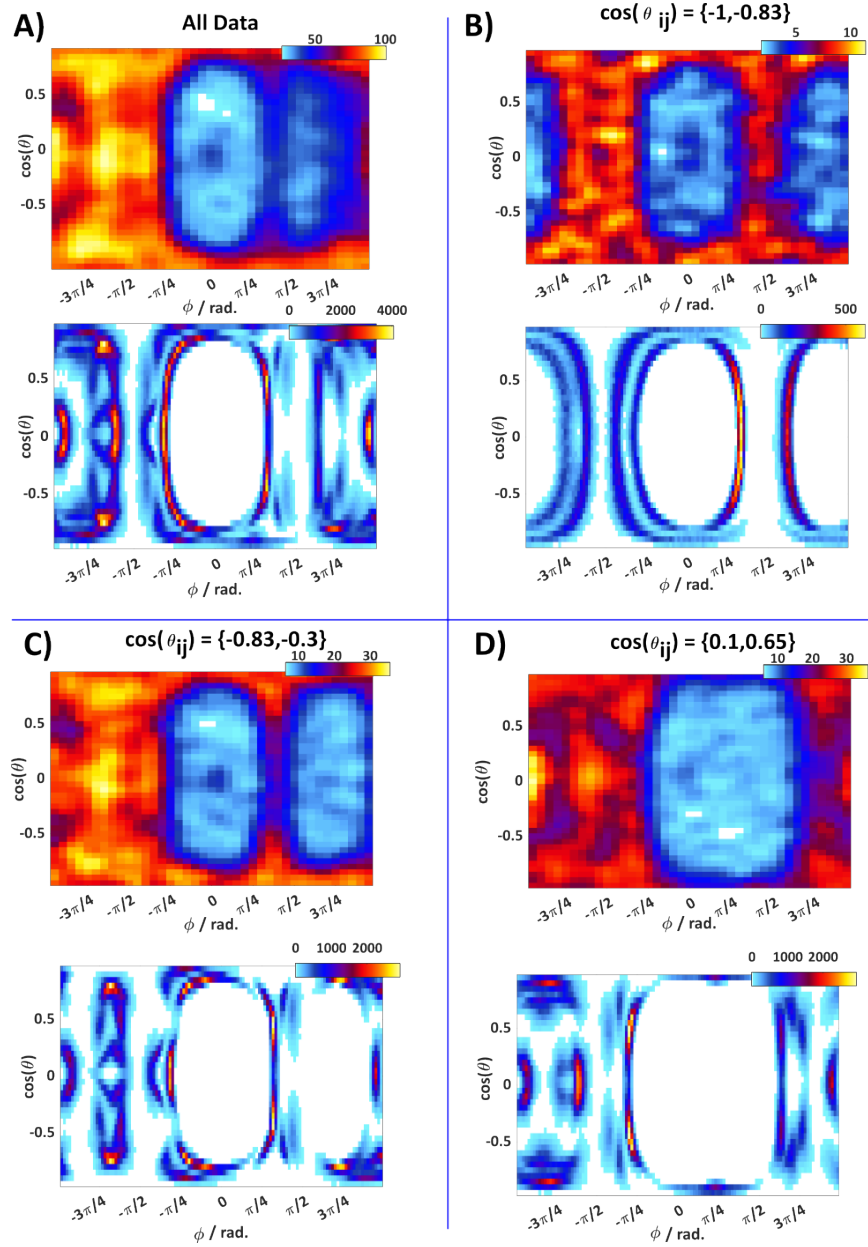


Figure 5.10: Angular distribution representation of the recoil frames that show the emission of ions relative to the elevation angle (θ) and relative to the direction of ion reference that defines the x -axis (ϕ). Measured data is the top plot of each panel, while simulated data is on the bottom. A) No reference selection. B) reference selection for nearly carbon sites emitted from opposite sides of the ring. C) Reference selection for second-nearest neighboring carbons. D) Reference selection for neighboring carbons. Data filtering is done in the same manner as figure 5.9.

references nor is it seen at this peak for these combinations. In a similar manner, the peak near $\phi \approx 3\pi/4$ occurs when the emitted ion sits near the reference ions, specifically the one closest to reference j (e.g., if $i = 5$ and $j = 4$, this is a signature of emission for carbon site 6). Lastly, signatures of emission from the opposite side of the ring relative to the reference ions are encoded at the peaks near $\phi \approx 5\pi/8$ and π . The ion will reciprocate between these two azimuthal peaks depending on the i,j - reference permutations. For example, if $i = 3$ and $j = 4$, then this peak will correspond to carbon-7, and occurs at $\phi \approx 5\pi/8$. Flipping the reference ions to $i = 4$ and $j = 3$ this carbon site occurs at $\phi \approx \pi$.

In conclusion, Coulomb explosion on a large non-planar cyclic molecule can reveal information about the molecular geometry. However, unlike the planar molecules, the corresponding images are much more complex and unintuitive for a non-planar molecule. Furthermore, when the cyclic molecule contains no preferential carbon sites, like the site for the methyl substitute in toluene, the number of reference ion combinations cannot be significantly reduced in the final Newton plot. However, as many of these cyclic molecules will emit their constituent ions with nearly equal kinetic energy, the Newton plots will have radial symmetry as the momentum distribution for all ions will have similar magnitude in this recoil frame, but emit in different directions. We have shown that by exploiting this phenomenon and looking at the recoil frame using the spherical coordinate angles relative to the xy -plane, specific ions relative to the references will have unique emission angles and site specificity can be achieved.

1,6-Heptadiyne

The successful mapping of molecular geometries from recoil frame momentum distributions via Coulomb explosion imaging has been demonstrated for two isomers of C_7H_8 , toluene and cycloheptatriene. The Newton plot for toluene is intuitive and reveals the constituent carbon configuration. A well-defined marker of the obstructed recoil of the single substituted carbon is observed even though it had identical mass-charge ratio as all other particles

detected in the coincidence experiment. Toluene’s planar geometry provides a good imaging in the xy -plane of the Newton plot, despite the 42 possible recoil frame combinations. Cycloheptadiene, although its imaging is much more unintuitive, had signatures of the ring geometry due to the reference-ion signatures in their relative angle distribution, and site specificity is enabled by reducing the observables to the emission angles of the carbon ions. However, these molecules are very rigid due to their cyclic nature. The ensemble of double bonds interconnecting all carbon sites prevents interconversion between different geometries. Thus prior to the X-ray interaction and subsequent charge up, the ensemble of molecules probed is assumed to be of a single geometry, and this is consistent by the experimental results.

We explore how the Coulomb explosion imaging method applies to non-cyclic molecules using the C_7H_8 isomer 1,6-heptadiyne as an example. This molecule contains no cyclic groups. Rather, it can be viewed as alkyne groups ($C \equiv CH$) bridged by ethyl groups ($CH_2 - CH_2$). The single bonds of these ethyl bridges facilitate easy rotation of the site groups about any molecular axis.

Figure 5.1 C shows a geometry that has C_{2v} planar symmetry, a similar motif to the toluene molecule. Here the symmetry point is located at the middle methylene site. In this geometry, the simulated Coulomb explosion image is intuitive. The breakup is confined to the xy -plane and the projected Newton plots onto this plane is reminiscent of the elongated molecular geometry. It contains signatures of obstructed breakup near the center of the plane, and anti-parallel emission with reference ions with the underlying diffuse features.

However, with the several single bonds, 1,6-heptadiyne and similar molecules can easily interconvert between different geometries, called conformers. Conformers are another category of isomers. The previous isomer pairs in this thesis can be categorized as geometric isomers, like the toluene and cycloheptatriene or the quadricyclane and norbornadiene pairs. The carbon sites have different bonds between them. It takes significant energy for them to interconvert, often necessitating excitation to a higher electronic state to overcome any

ground state potential energy barriers.

Now, for molecules like for 1,6-heptadiyne, the molecule can have several different geometric configurations. They are defined with the *gauche* and *anti-gauche* orientations, in which the ethylene substituents sit on the same or opposite side of the symmetry plane, respectively. These molecules can easily interconvert to different conformers by rotation about the single bonds. Generally, interconversion can take place thermally as the barrier between these different configurations is low, typically on the order of 200 meV for these types of hydrocarbons¹⁶⁶. Thus, the symmetry and planar properties between conformer configurations can vary greatly.

Figure 5.11 includes the simulated results of Coulomb exploding an admixture of different conformers of 1,6-heptadiyne. For a sample temperature as low as 2 Kelvin, we expect two primary conformers: GG-trans ($\sim 81\%$) and AG ($\sim 16\%$) with all other conformer configurations being negligible¹⁶⁷. The simulated Coulomb explosion image changes greatly compared to the AA case shown in fig. 5.1 I. Here, there is no symmetry in the xy - plane. The xz - and yz - plane contains significant mirror symmetry about the xy -plane with all features off axis, showing no sign of anti-parallel emission from the reference ions.

The unintuitive nature of these simulated results provides insight to the experimental results. As shown in fig. 5.1 F, the Newton plots from the measured spectra is a structureless distribution in all 3 planes. As the experimental data is unable to resolve finer details in the Coulomb explosion imaging patterns, exemplified by the results of the previous two isomers likely due to inadequate resolution or deviations from the assumed prompt charge up and explosion process, we might expect this with the several fine structures in the Newton plot for the conformers. More importantly however, the ratio of conformers could vary significantly from the one reported in literature literature¹⁶⁷, as the uniform sample temperature of this system is expected to be significantly warmer with 10s of Kelvin. As the ratio of conformer geometries varies drastically at low temperature, it is likely that our experimental measurement is comprised of several more conformer geometries than assumed.

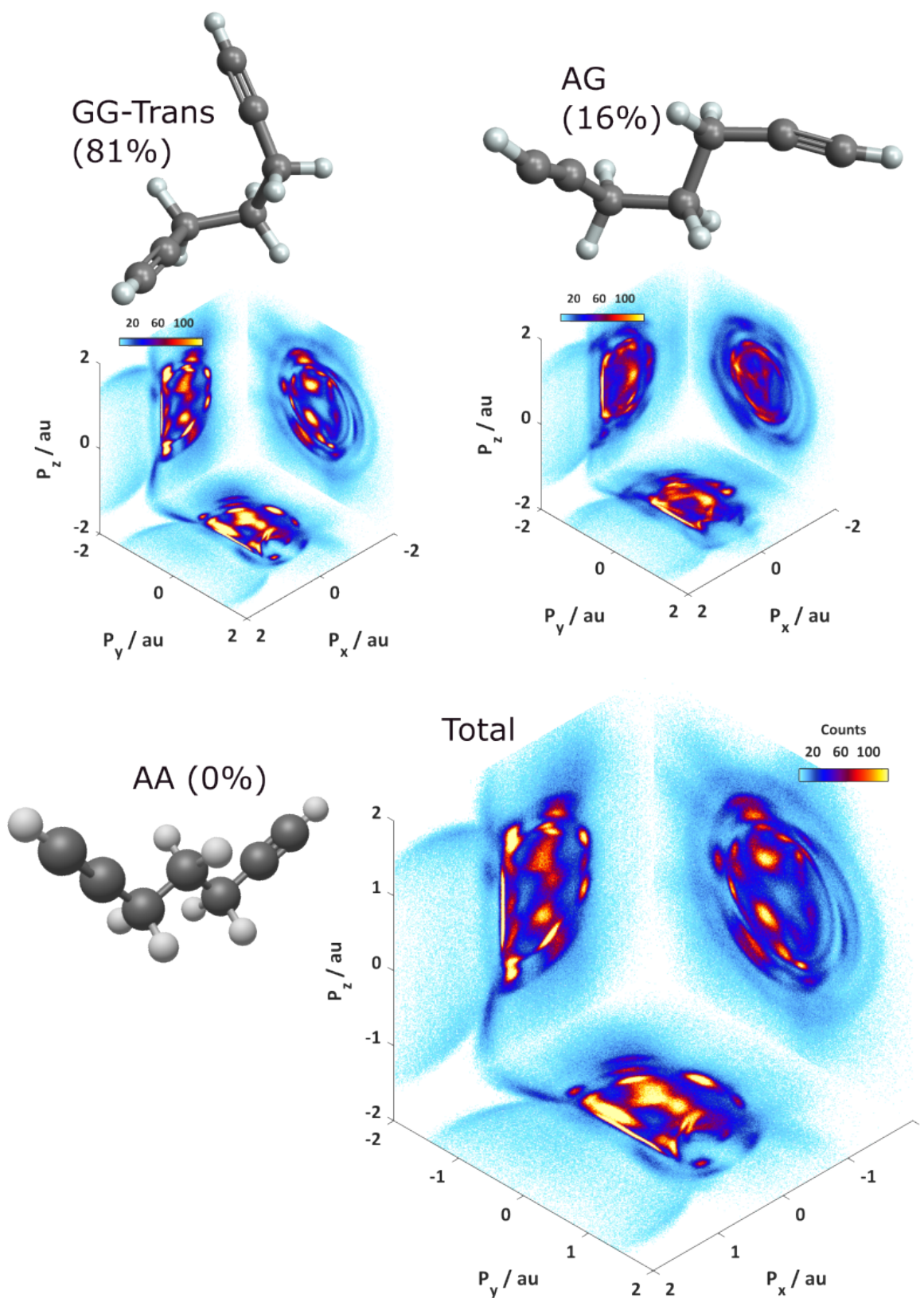


Figure 5.11: *Coulomb explosion imaging simulation for expected conformers of 1,6-heptadiyne.*

5.4 Methods

In this section, we outline the experimental setup and analysis methods employed for these CEI studies. Coincidence ion momentum measurements and Coulomb explosion imaging are high-dimensional measurements, requiring several steps of data processing. These steps are outlined below.

The repetition rate of the EuXFEL is 10 Hz. The machine operates in a burst mode, where within each separate electron bunch in the injector, there are equally spaced electron pulses with 1.1 MHz spacing. Every sixth pulse was used to generate the X-ray pulse. Due to limitations of the machine, including the ion time-of-flight spectroscopy technique that requires adequate spacing between each shot so slow ions can reach the detector before the next X-ray ionization event, the effective repetition rate was 600 Hz. The X-ray photon energy was 1.5 keV, selected to probe above the carbon K-edge. This high photon energy enables a smaller focus, which is desired for higher intensity to drive non-linear photoabsorption processes.

The single-shot average pulse energy was approximately 4 mJ, as measured by an upstream gas monitor detector. The estimated fluence attenuation from the Kirkpatrick–Baez mirrors is $\sim 80\%$, resulting in an estimated 3.2 mJ pulse energy at the interaction point. The x-ray beam steering and spot size were controlled by a pair of KB mirrors and the focus spot size is estimated to be $1.4\ \mu\text{m}$ diameter FWHM. The pulse duration is estimated to be 25 fs based on the 250 pC electron bunches. There was no direct measurement of the X-ray pulse duration at the time of this experiment.

All three molecular samples were delivered to the interaction point in the same way. The liquid sample was loaded into an out of vacuum stainless-steel reservoir. The high vapor pressure for all three molecules at room temperature granted adequate sample density without heating or a carrier gas (Toluene at 40 millibarr¹⁶⁸, cycloheptatriene at 20 millibarr¹⁶⁹, and 1,6-heptadiyne at 30 millibarr¹⁷⁰). The sample vapor was delivered into the vacuum chamber through a $200\ \mu\text{m}$ flat nozzle for adiabatic expansion. The gas jet consists of three

pumping stages separated by sub-millimeter skimmers to select the coldest section of the collimated jet. The sample volume size at the interaction point was controlled by cutting the gas jet with three piezoelectric skimmers, with a selected $500\ \mu\text{m}$ spacing.

The spectrometer assembly has been discussed at length in section 3.2.2. In the configuration for this experiment the spectrometer length was 25 cm in total. The extraction length was 15 cm with a 4 kV voltage drop across this region for an estimated uniform spectrometer field of $235\ \text{V}/\text{cm}$, as shown in fig. 3.8.

The photoions were detected with a 120 mm diameter MCP and hex-anode assembly¹⁷¹. The latter contains 6 reciprocating wires to determine the particles position, as described by the procedure in 3.2.2. A voltage of $-2.5\ \text{kV}$ was applied to the front of the MCP while the anode was held at ground.

Figure 5.12 shows an example of the data pipeline for determining the ToF and positions of the photoions from the raw signals read from these detectors. These signals were recorded with a fast digitizer. An example analogue waveform is shown panel A. The data was binned by selecting arrival times of the hits using a software constant-fraction discriminator. Six example hits are shown in panel B. While the arrival-time difference between signals at the ends of the wire would vary depending on the position, the time-sums should be constant regardless of the particles position it lands on the detector after adding the flight-time. However, as seen in panel C, this relationship delineates significantly and can cause incorrect sorting of positions between several ions. The function of the time sum versus position can be corrected, as shown in panel D, enabling correct assignments of coincident particles positions and ToFs. Furthermore, with the hex-anode having a redundant third wire, a few signals can be missed, but their values can still be reliably reconstructed. Figure 5.12 provides an example synopsis of these reconstructions, tabulating all possible 19 missing-signal permutations. Reconstruction 0 (which contains nearly 80% of all events), is the case where all arrival times are measured (2 for both ends of the three wires, and 1 for the MCP, as denoted by the top axis). The total detected ion rate was 4 hits per shot, with 2 hits

per shot contributing from background events. See reference¹⁷² for more details of this data pipeline.

The ionic species generated from x-ray ionization were determined through standard ion time-of-flight calibration, where the ion flight times are proportional to the square-root of their mass-to-charge ratio, $ToF \propto \sqrt{m/q}$. The ToF spectra for all three samples are shown in fig. 5.13. A great deal of fragmentation occurs through multiphoton x-ray absorption, and these three isomers break up with nearly identical yields for all fragmentation species.

Figure 5.14 shows an example position versus ToF spectra for toluene. The red line shows any subtle shifts in the position distributions that would signify offsets from the supersonic gas jet. The x -position is notable for the long U-shaped features that extend over the entire detector diameter for each ionic species. These are due to the X-ray source being able to ionize any background outside of the focus as it propagates along the x -direction. For initial coincidence data analysis, the data was reduced by selecting events that fell in a broad ToF window that corresponds to ionic species of C^{2+} , $ToF \in \{0.825, 0.972\} \mu s$.

After binning the data into ToF and position values on a single shot basis, shots with three or more detected particles were selected. All hits within a shot were permuted into groups of three. This accounts for false coincidence particles that may land between two real particles in time-of-flight, where a permutation with this false coincident particle would be removed via momentum filtering methods described below. The coincidence channel selected for the data in this thesis are all identical ion species with the same mass-to-charge ratios. To avoid biasing any coincidence spectra, especially when defining the reference ions for the recoil frame, we randomly resort all these hits in the same shot.

The particle momentum is calculated using standard kinematic equations of charged particles in uniform electric fields. With the measured values x and y -positions in the lab frame, and time-of-flight for the i^{th} particle detected (x_i, y_i , and ToF_i , respectively), the momentum can be calculated using the following equations:

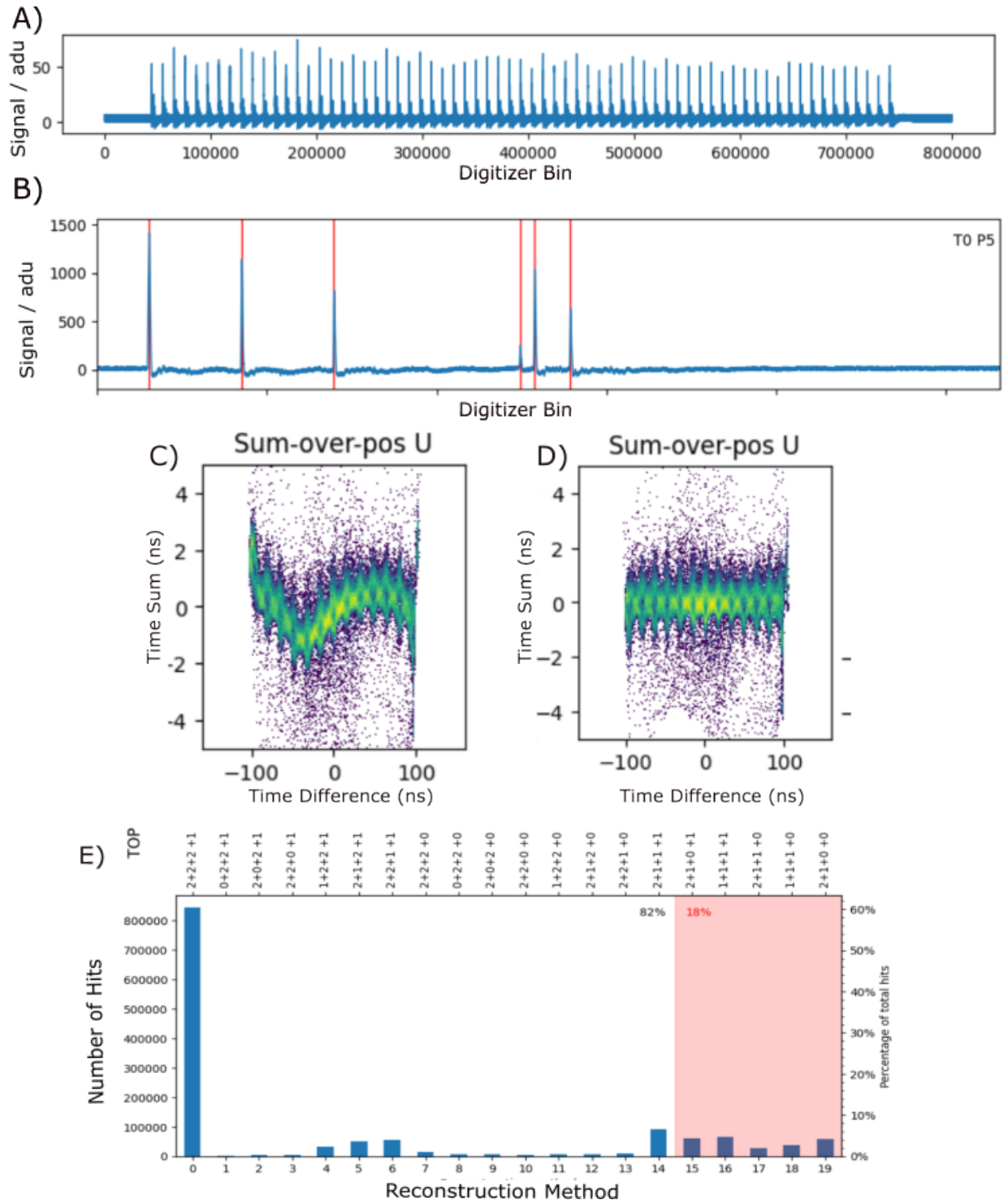


Figure 5.12: Routine for hex-anode reconstruction A) Example waveform from a delay-line detector. B) Zoomed-in waveform within narrow timeframe to observe individual peaks found through software CFD routine. C) Time sum of arrival times at the two ends of a delay-line wire against the timing-difference, which directly maps to the position of the detector. D) Non-linearity correction applied to data in panel C. E) Reconstruction synopsis for dataset.

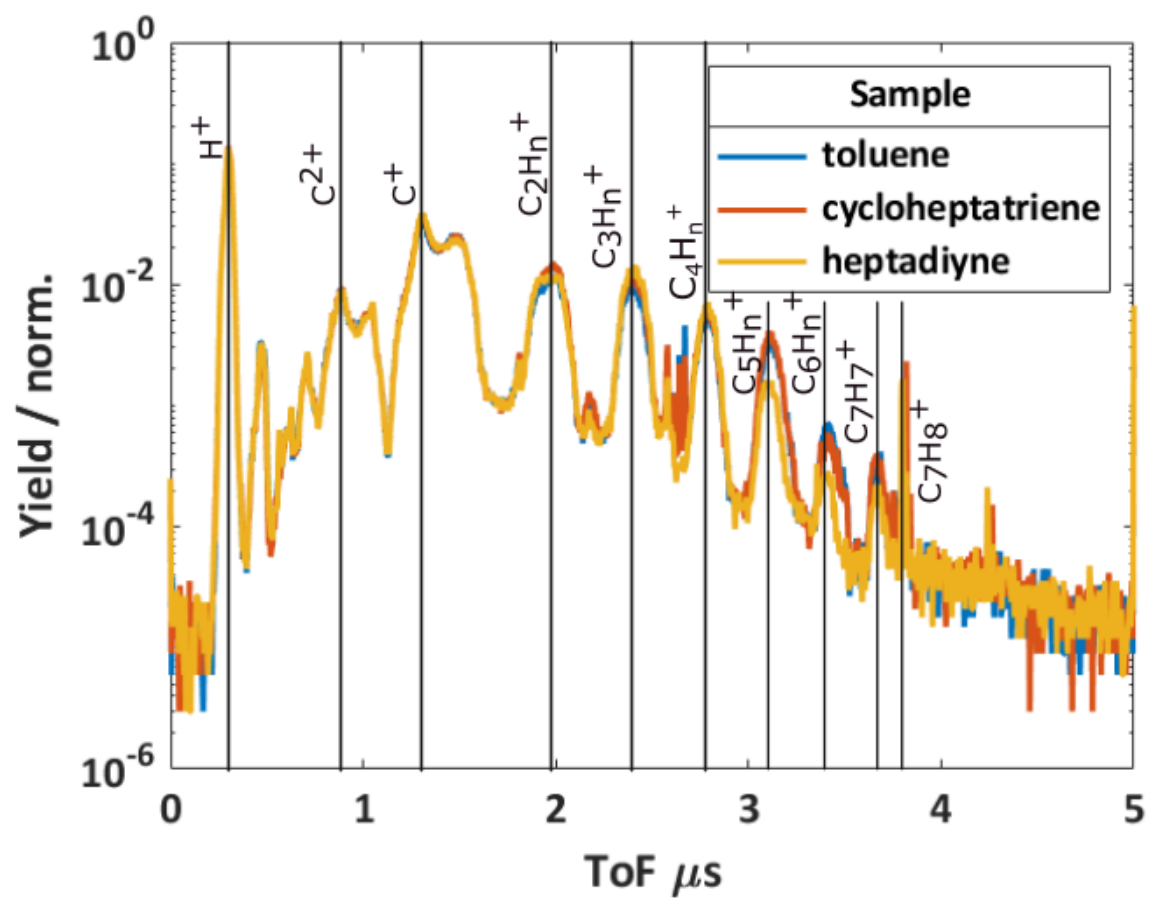


Figure 5.13: Time-of-flight spectra of Coulomb exploded C_7H_8 isomers. Daughter ionic species are labeled in groups of number of carbons.

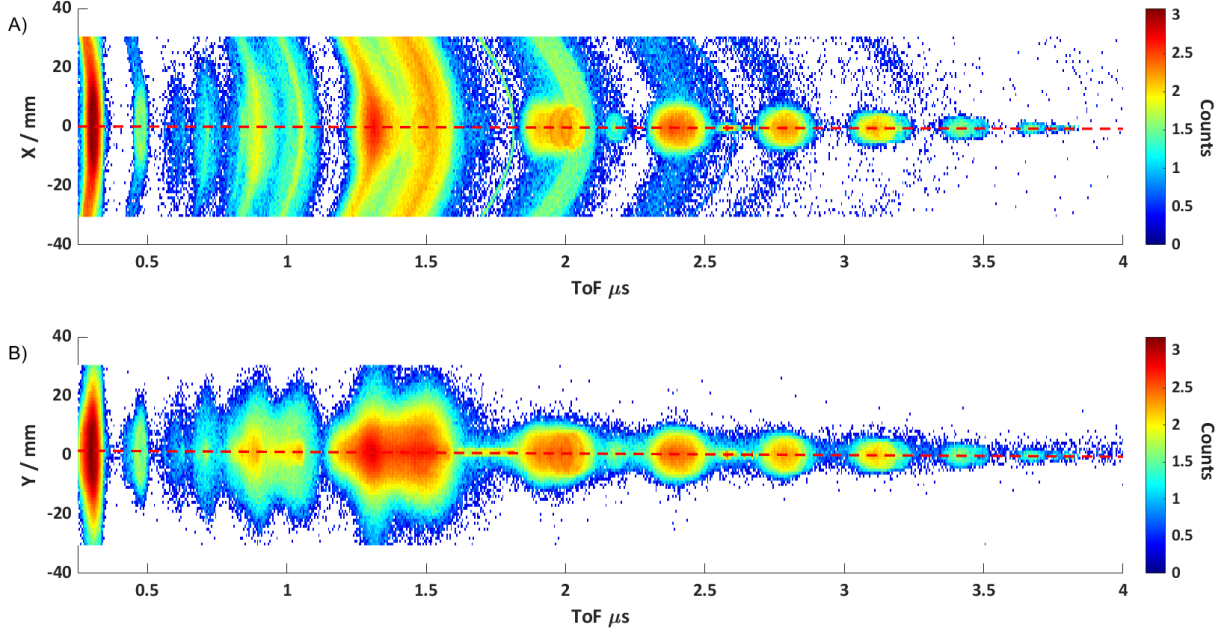


Figure 5.14: *Position versus Time-of-Flight spectra for Toluene.*

$$\begin{aligned}
 P_{ix} &= m_i \left(\frac{x_i - x_0}{ToF_i - t_0} - V_{0x} \right) \\
 P_{iy} &= m_i \left(\frac{y_i - y_0}{ToF_i - t_0} - V_{0y} \right) \\
 P_{iz} &= \frac{q_i V}{2 \left(l + \frac{1}{2}d + z_0 \right)} (ToF_i - t_{i0}) - m_i V_{0z},
 \end{aligned} \tag{5.1}$$

Here m_i and q_i are the mass and charges of particle i , while t_{i0} is its central ToF value, defined as the ToF value where the particle would have no initial momentum along the ToF axis. Values x_0 , and y_0 are the coordinates of the interaction point relative to the center of the detector, these position values can be obtained by observing the offsets in the measured positions to the center of the detector. The jet velocity values are V_{0x} and V_{0y} , which can be determined by observing the linear dispersion of the central position of different fragment species at their respective ToF values (the red line spanning the horizontal axis in fig. 5.14 shows an example of this).

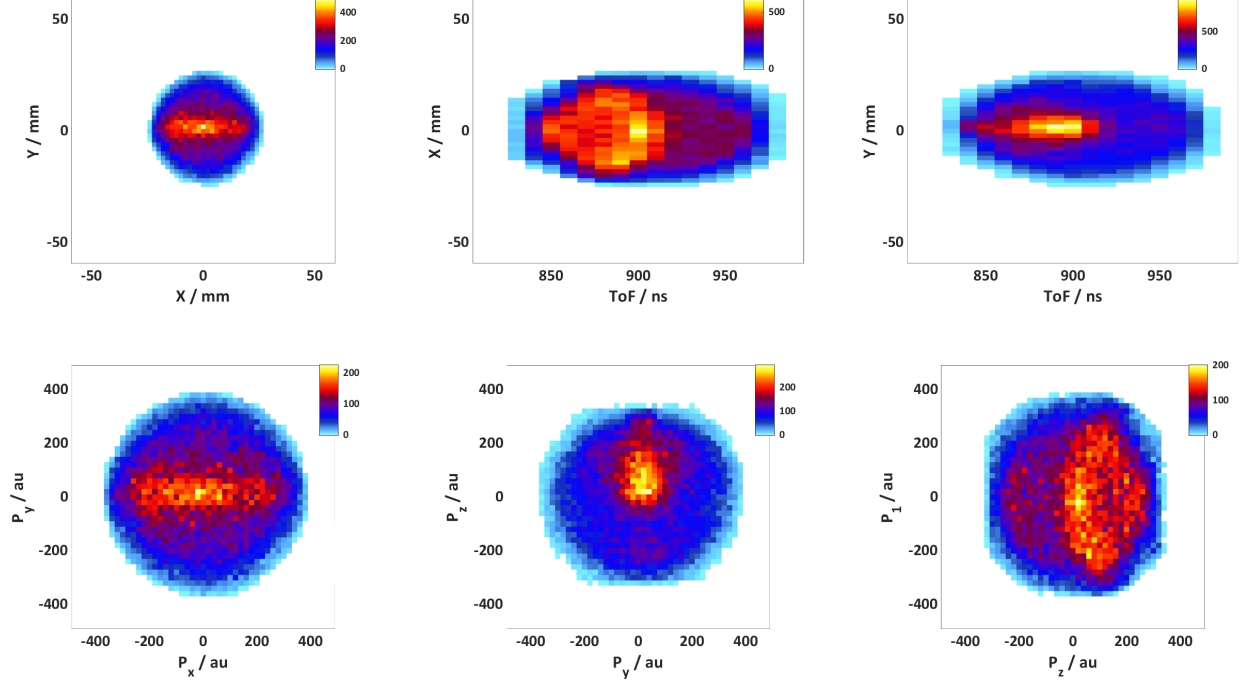


Figure 5.15: *Top row: position and time-of-flight for gated ionic fragments corresponding to C^{2+} in Coulomb exploded toluene. Bottom row: corresponding momentum derived from eq. 5.1*

The constants in the equation for P_{iz} relate to the spectrometer geometry, with l and d are the spectrometer and field-free drift length respectively, which are known values. Meanwhile z_0 and V_{0z} are the offsets of the interaction point and jet velocity. The latter two are found best by tuning their values such that the momenta distribution along the z -direction is centered at zero and the width of the distribution best matches those for the momentum in x - and y -direction. The distribution of these momenta and position after filtering are shown in fig. 5.15.

As these measurements are kinematically incomplete, meaning we are only accounting for 3 ions detected when up to 15 ions could be generated in the X-ray ionization, the measured total momentum will be very broad, although centered around zero. Other factors increase the total momentum distribution width, including detector position resolution. Additionally, the constants corresponding to jet velocity (V_0) and interaction positions (x_0, y_0, z_0) in eq.

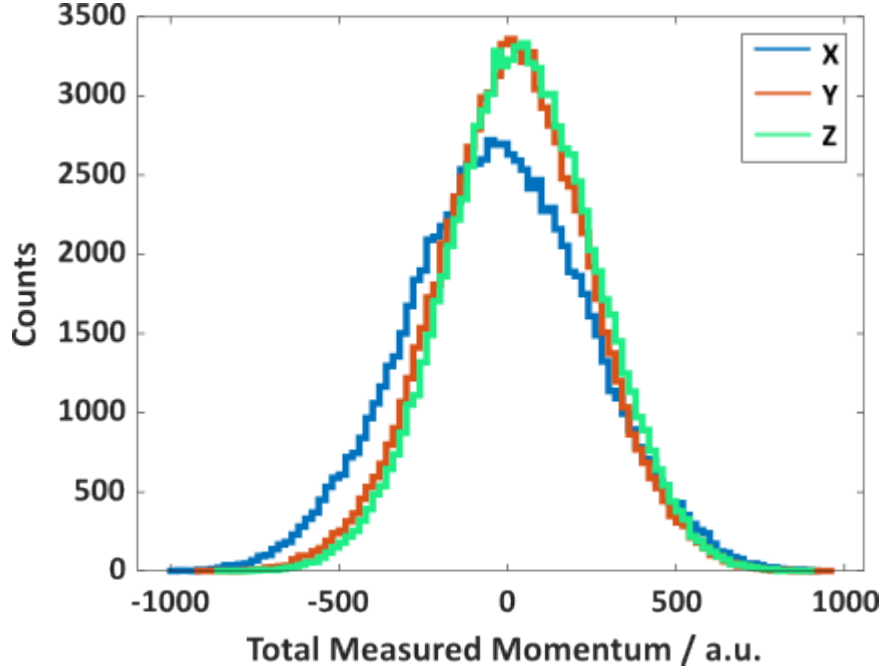


Figure 5.16: *Measured momentum sum for all three directions for three particle coincidence channel for ionic fragments of C^{2+} .*

5.1 would not have the same value for every molecule probed, but would rather have a distribution according to the jet temperature and focal interaction volume size. Lastly, the high electron kinetic energies from soft X-ray absorption and the Auger-Meitner electrons (around 250 eV for these hydrocarbons¹⁷³) will carry non-negligible momenta that are not measured (on the order of 10 a.u. for both).

Exemplary momentum distributions are shown in fig. 5.16.

For verification of the calibration parameters, we measure the kinetic energy release of molecular nitrogen forming the $N^+ + N^+$ coincidence channel. Figure 5.17 shows the results, which are in good agreement for central-peaks positions measured data with 419.3 eV photons using a COLTRIMS spectrometer¹⁷⁴.

With the center-of-mass defined, preparing the recoil frame is straightforward. As discussed in section 5.3, this reference frame is used to visualize the molecular breakup on a plane defined by the measured momentum of two particles. It is a rotation operation that points selected reference ion- i momentum along the horizontal axis (denoted by unit

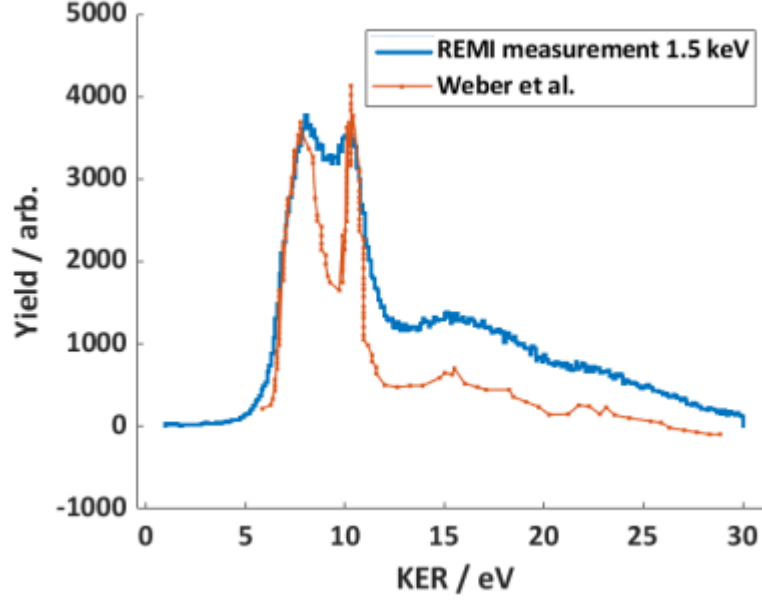


Figure 5.17: *Kinetic energy release for $N^+ + N^+$ coincidence channel in comparison to measurement with 419.3 eV photon and COLTRIMS type spectrometer¹⁷⁴.*

vector $\hat{u}$), and a component of the second reference ion- j momentum, the perpendicular component to the former, along the vertical axis (denoted by unit vector $\hat{v}$). The direction out of the recoil plane will be the cross-product of these two unit vectors (denoted by unit vector $\hat{w}$),

$$\begin{aligned}\hat{u} &= \frac{\vec{P}_i}{|\vec{P}_i|} \\ \hat{v} &= \frac{\vec{P}_j - (\vec{P}_j \cdot \hat{u}) \hat{u}}{|\vec{P}_j - (\vec{P}_j \cdot \hat{u}) \hat{u}|} \\ \hat{w} &= \hat{u} \times \hat{v}.\end{aligned}\tag{5.2}$$

The recoil-frame momenta of the ion- k , which will have three components in this frame, are then calculated by taking the dot product with these unit vectors. By convention, the momenta is scaled by dividing the magnitude of $|\vec{P}_i|$.

$$\vec{P}_k' = (\vec{P}_k \cdot \hat{u})\hat{u} + (\vec{P}_k \cdot \hat{v})\hat{v} + (\vec{P}_k \cdot \hat{w})\hat{w} \quad (5.3)$$

Lastly, the numerical Coulomb explosion simulations were performed by solving 3N coupled differential equations for the particles undergoing the Coulomb explosion process. All ions in this simulation were assumed to have no initial velocity, and their initial positions were determined by their molecular coordinates. The system of equations was the standard Newton's second equation under the Coulombic force:

$$m_i \frac{d^2}{dt^2} \vec{r}_i(t) - \sum_{j=1}^N q_i q_j \frac{\vec{r}_i(t) - \vec{r}_j(t)}{(\vec{r}_i(t) - \vec{r}_j(t))^{3/2}} = 0 \quad (5.4)$$

To best model the experimental data, all carbons were doubly charged ($q = 2$) and hydrogens were singly charged ($q_i = 1$). These equations of motion were solved out to 10^7 atomic units of time using Mathematica's numerical differential solver package NDSolve¹⁷⁵.

5.5 Conclusion

This section has illustrated that X-ray induced Coulomb explosion imaging is an effective method for probing the molecular geometry of pure hydrocarbons. For these systems there is no preferential absorption site, nor can one define a single recoil frame from the experimental data as there are no unique atomic sites in the molecule that can act as references for momenta of other ions. However, as the coincidence momentum measurements provides several metrics for these non-unique reference ions, it is possible to select events where only a certain combination of site-specific reference ions contribute. In this chapter we showed several examples using the angular distribution between these reference ions or their respective kinetic energies.

The results in this section further prove the efficacy of Coulomb explosion imaging for all sorts of scenarios. CEI has already been proven suitable for imaging molecules with

two or more unique atomic sites^{1,176}, and even a single unique site for symmetric planar molecules, the latter geometry even being probed as it undergoes ultrafast ring opening¹⁷⁷. Unlike diffraction-based imaging methods that can only represent geometries by relative distances between atomic sites with no angular discretion, CEI can provide an intuitive three-dimensional representation of the molecular geometry. Additionally, as shown in this section, the underlying assumptions of occupation of highly charged states and instantaneous explosion have proven adequate experimentally and are easy to simulate.

Although the ultimate goals for distinguishing different hydrocarbon isomers using CEI are met, the clarity of the experimental images can certainly be improved. The primary reason is low statistics, as the effective FEL repetition rate is low. Additionally, the ion detection rates are unreasonably high with an average of four hits per shot, where generally running well below one ionization event per shot is preferred in order to reduce the contribution from false coincidences. Thus, the next generation high repetition rate sources will revolutionize this technique, such as the megahertz LCLS-II or commercially available 100 kHz tabletop sources.

Although CEI has been utilized for decades, it still has great developments ahead for experimental, analytical, and theoretical methodologies. These include utilizing covariance methods for when the measurements for higher detection rates^{178,179,180,69}. Additionally, advanced theory that incorporates x-ray molecule interaction and charge-up process are being developed and are guiding interpretation¹⁸¹. CEI is proving a promising candidate as the most direct- unambiguous imaging method for studying the time evolution of molecules.

Chapter 6

Conclusion and outlook

For the projects in this thesis, we set out to study the structure and dynamics of molecular systems that have potential applications for molecular photoswitches, energy storage, or other systems where photoinduced isomerization is important. The structural and dynamical properties of these molecules were probed via XUV or X-ray ionization, and the kinetic energy of the electrons or correlations in the three-dimensional momenta of the ions provided the observable.

Chapter 2 discussed the theory of molecular photoexcitation ionization wavepacket dynamics that are relevant to our time-resolved experiments. These experiments employed Free-electron lasers for intense XUV or X-ray light pulses as the ionizing sources, as discussed in chapter 3. There, we elaborated on the different FEL sources used in this work, including the SASE and seeded methods and discussed strengths and limitations of the two. The photoparticle detection methods were discussed extensively, including the characteristics of the reaction microscope for ion-coincidence momentum imaging.

Two experiments in this work were performed with magnetic bottle electron spectrometers, one for time-resolved XUV photoelectron spectroscopy (chapter 4), and the other for time-resolved near edge X-ray absorption spectroscopy (section 3.5).

Characterization measurements on a magnetic-bottle spectrometer were done and the

results are included in the manuscript in section 3.4, which demonstrate this instrument’s good resolution for photoelectron spectroscopy. There, we also discussed a ubiquitous periodic modulation artifact in the MBES time-of-flight spectra caused by detected electrons undergoing cyclotron motion, and an algorithm to correct for it.

Several results on detector correlation measurements akin to traditional ghost-imaging for improved resolution from noisy SASE FELs were shown in sections 3.3 through 3.5. Particularly, we discussed a new method to employ a time-domain ghost-imaging technique to improve the temporal resolution when measurements are performed with slow acquisition detectors unable to operate at beam rate, and would thus be unable to correct for variations in the pump-probe delay on a single shot-basis.

Chapter 4 contained the results of an experiment and theory collaboration that monitored the relaxation pathways of photoexcited quadricyclane, one of the most promising candidates for molecular solar-thermal energy storage systems. The measurement revealed the importance of two different relaxation pathways, a fast ‘valence’ and a long lived ‘Rydberg’ relaxation pathway, with the latter being unexplored in previous work. This experiment demonstrated the importance of employing XUV ionization in time-resolved photoelectron spectroscopy, as it enables the observation of fast valence pathways all the way to the ground state. The non-adiabatic molecular-dynamics simulations were in good agreement with the experimental observables and guided our understanding the TRPES, especially for the time constants that are extracted from global-fitting methods. This measurement enabled studying molecular dynamics upon relaxing to the ‘hot’ ground state, and timescales of photoproduct formation were extracted. Evidence of photodissociation in the ground state were revealed.

The molecular systems studied in chapter 5 were more for pragmatic development of Coulomb explosion imaging rather than their application in optical photoswitches. The Coulomb explosion imaging of three different isomers of pure hydrocarbons with seven carbons was explored. These molecules included a substituted six-membered molecular ring, a

non-planar seven membered ring, and a non-cyclic molecules with several possible conformer geometries. Unlike previous work employing FEL X-ray induced CEI, these molecules had no unique absorption sites nor unique atomic constituents that could build a recoil frame of reference to represent the Coulomb explosion process. Rather, the recoil frame contained all possible combinations of the identical ion momenta. Although the corresponding Newton plots were distinguishable between all three isomers, without further analysis they were unintuitive and contained several features that could not map to the molecular geometry. But the strength of CEI is that its high-dimensionality provides several metrics facilitating data filtering. When selecting certain correlations between the reference ions, the composite recoil-frames in the final Newton plot could be reduced, resulting in clearer data that could map to molecular geometry. The results were greatly aided with a simple coulomb explosion simulation. This chapter also discussed the capability of employing CEI to map the Newton plot observables for non-planar cyclic molecules by exploiting the nearly equal energy of all emitted particles, which makes the Newton plots nearly radially symmetric, and the recoil frame momentum correlation could be visualized in a two-dimensional angular distributions, rather than complex three-dimensional Newton plots. This section did discuss the inability of Coulomb explosion imaging to identify the molecular geometry when the signal contained several contributions of conformer geometries. However, CEI has proven successful for conformers of much smaller molecules with preferential absorption sites¹⁴⁵.

All of the work in this thesis was part of a large collaboration with several other scientific groups approaching similar problems, and several projects are still ongoing that will further elucidate the results in this thesis. Particularly, the relaxation dynamics of photoexcited norbornadiene were measured with identical experimental setup in chapter 4. Also, as one of the main observations from the quadricyclane measurements was the very different Rydberg states populated when the pump-photon energy was different by just 10 nm, measurements in Rydberg fingerprint spectroscopy as a function of pump-wavelength have recently been measured and are currently being analyzed^{182,116}. For validation of

the conclusion of ground state dynamics in this thesis, especially for signatures of product formation and fragmentation, time-resolved electron and x-ray diffraction measurements on quadricyclane and norbornadiene are being analyzed. These forthcoming results will be much more appropriate to assign geometric structure of the photoproducts than the photoelectron spectroscopy employed in this thesis.

Additionally, huge advancements in X-ray free-electron lasers are under development, especially with the recently commissioned LCLS-II which is anticipated to go to a megahertz repetition rate. This high repetition rate will enable much more sophisticated measurements with better signal-to-noise, and photoparticle spectrometers are in development to take advantage of this at the Time-resolved AMO endstation (TMO). The magnetic bottle spectrometer discussed in section 3.4 is being equipped with an ion detector to perform electron-ion covariance measurements. Also the *Dynamical REAction Microscope* (DREAM) spectrometer is being built¹⁸³. This spectrometer is similar to the one used in experiments in chapter 5 and enables similar Coulomb explosion imaging measurements at 100s of kilohertz repetition rates. Lastly, a multi-TOF spectrometer, called *Multi-resolution Cookiebox* is currently being commissioned¹⁸⁴. This device will enable non-invasive single shot spectral, temporal, and polarization characterization of the MHz FEL source^{185,186,187,77}.

The work presented in this thesis includes several experimental methods to distinguish complex isomers and monitor their photoexcitation dynamics. We have demonstrated that methods like time-resolved photoelectron spectroscopy and Coulomb explosion imaging are powerful tools to provide a general understanding of their isomerization processes. The methods in this thesis, especially free-electron lasers, continue to be developed, opening up new possibilities for studying these and even more complex molecular systems. The outlook of implementing the fundamental science these measurements have uncovered for application in the energy or information sector is promising.

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