

Imaging photo-induced dynamics in halomethane molecules with coincident
ion momentum spectroscopy

by

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Abstract

Molecular transformations triggered by the absorption of light are of tremendous importance in our day-to-day life, science, and technology. Examples of such “photo-induced” reactions include, among many others, photosynthesis, solar energy conversion, and mechanisms behind human vision. Besides knowing the final outcome of such reactions, for many scientific and technological applications it is crucially important to understand how they evolve in time, and how the motion of individual atoms leads to a certain outcome. For decades, resolving these processes in time represented a severe experimental challenge since the atomic motion involved is extremely fast. The availability of ultrashort, femtosecond laser pulses in combination with novel molecular imaging techniques provides experimental tools needed to address this challenge.

This thesis describes the application of coincident ion momentum imaging setup, sometimes called “a reaction microscope”, for studies of photo-induced dynamics in halomethane molecules (CH_2I_2 , CH_2ICl , CH_3I). The main objective of this work is to visualize light-induced breaking, rearrangement and formation of molecular bonds, and to determine relevant mechanisms and time scales. Halomethanes are often considered as model systems for studying such prototypical photochemical events because they are small enough to allow for reasonable electronic structure calculations and for coincidence detection of all molecular fragments, while being large enough to be of chemical relevance and to undergo some fundamental chemical transformations. The work described here covers three different regimes of light-molecule interaction: (1) ionization and fragmentation by an intense near-infrared (NIR) field, (2) excitation of a neutral molecule by a single ultraviolet (UV) photon; and (3) ionization and fragmentation by a single extreme ultraviolet (XUV) photon. We specifically focus on several aspects of halomethane photochemistry that are of general importance, have

been actively discussed in literature, and yet are difficult to access using more established imaging or spectroscopic techniques.

More specifically, we first characterize molecular response to a single intense femtosecond NIR pulse at 800 nm, identifying and disentangling different ionization and fragmentation channels, and their signatures in various coincident observables. Then we apply multiple ionization and rapid dissociation (“Coulomb explosion”) by such a pulse as a tool to map molecular dynamics in pump-probe experiments. In this approach, the information on molecular geometry at the time when the probe pulse arrives is extracted from the coincident measurement of the 3D momentum vectors of the detected fragment ions. We start with the NIR pump / NIR probe experiments on CH_2I_2 and CH_2ICl molecules, aimed at characterizing bound and dissociating wave packets induced by a strong NIR field. Here, we find that both, dissociation dynamics and molecular halogen elimination (I_2 or ICl) are mainly governed by the large-scale bending vibrations of the molecule, even though (weak) signatures of stretching vibrations can be also observed in the spectra. Focusing on the I_2 (or ICl) elimination channel, which requires breaking two carbon-halogen bonds and formation of a new bond between the two halogen atoms, we demonstrate how it can be disentangled from the other fragmentation channels, and find that it is dominated by a direct, “synchronous” pathway.

Then we apply the same approach and the same NIR probe pulses to study the photoexcitation of diiodomethane (CH_2I_2) by a femtosecond UV pulse at 266 nm in a UV pump / NIR probe experiment. Here, in addition to two-body dissociation and I_2 elimination channels, we also observe a significant contribution of three-body dissociation. This channel can be easily separated in our triple-coincidence measurements, but is notoriously difficult to identify with most of the other techniques. Besides that, we find signatures of transient $\text{CH}_2\text{I-I}$ isomer formation within the first 100 femtoseconds after the initial photoexcitation. While the picosecond-scale isomerization of CH_2I_2 was clearly demonstrated earlier in the liquid-phase experiments in solution, and was shown to occur due to the interaction with the solvent, the existence of a much faster, intra-molecular isomerization pathway for isolated molecules in a gas phase was debated in literature. In this work, we provide direct evidence

of such ultrafast, sub-100 fs CH_2I_2 isomerization, and demonstrate that the decay of this short-lived isomer opens up an additional pathway for molecular iodine elimination.

Finally, we have performed a complementary study on CH_2ICl and CH_3I molecules employing short extreme ultraviolet pulses (XUV) from FLASH II free-electron laser facility in Hamburg, Germany. Here, one femtosecond XUV pulse at ~ 53 nm central wavelength is used to initiate the dynamics, mainly by single-photon ionization, while the second identical pulse is used to probe the evolution of the created ionic-state wave packets. Employing the same ion momentum imaging setup, we map different dissociative ionization channels and observe signature of intramolecular electron transfer between different sites of a dissociating molecular ion. In contrast to the results of earlier FEL experiments on X-ray inner-shell photoionization of dissociating halomethanes, which could be readily explained using the classical over-the-barrier charge transfer model, our data for valence XUV ionization suggest a more subtle dependence of the charge transfer probability on the internuclear distance, likely determined by the delocalization of molecular orbitals.

Overall, the work presented in this thesis advances our understanding of different pathways in strong-field and single-photon induced photochemistry of halomethanes, and demonstrates an efficient and visual approach for mapping transient reaction intermediates. The tools and methodology presented here can be applied to study a broad range of ultrafast photochemical reactions, and can be useful for many strong-field imaging and control applications.

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Major Professor
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Last but not least, there is one person who has always encouraged and shared my emotions in my ups and downs and has always encouraged me, my wonderful and amazing wife, Sushma Parajuli.

Dedication

To my daughter Aarya, son Aaron, wife Sushma and my parents.

Chapter 1

Introduction

Molecular response to the absorption of light plays a central role in numerous physical, chemical and biological processes. It includes many natural light-induced phenomena crucial for our day-to-day life, like photosynthesis [1], retinal cis-trans isomerization in vision [2] or bio-synthesis of pre-vitamin D [3], and provides a basis for a broad range of scientific and technological applications. A detailed understanding of such photo-induced reactions is one of the important tasks for chemical physics, physical chemistry and certain areas of biophysics. A traditional way to study photochemical processes focuses on initial reagents and final reaction products, similar to other sub-fields of chemistry. While both the initial and the final states of a reaction are usually well characterized, information on what happens in between is often lacking. This knowledge can be particularly important if there are several possible pathways leading to the same final state. Since the essential steps for many chemical reactions occur on the timescale of few femtoseconds to hundreds of femtoseconds ($1 \text{ fs} = 10^{-15} \text{ seconds}$), determined by the motion of atomic nuclei, to study their evolution in time tools capable of resolving such ultrafast time scales are needed. For reactions triggered by light, these tools can be provided by ultrashort lasers. Since the early 1980s, when rapid evolution of laser technology made lasers with sub-picosecond pulse durations routinely available [4] [5], these lasers had been used to study the dynamics of numerous reactions, forming a new field named femtochemistry [6] [7]. The founder of this field, Ahmed Zewail,

was awarded the Nobel Prize in chemistry in 1999 “for studies of the transition states of chemical reactions using femtosecond spectroscopy” [7] [8].

A comprehensive picture of a photochemical process in a single molecule needs to combine information on its evolving electronic structure and on the motion of its constituent atoms following interaction with light. A lot of information on “static” electronic structure and nuclear geometry of molecules can be obtained from various high-resolution spectroscopic techniques (e.g., absorption, fluorescence and photoemission). While these approaches are typically less efficient for studying ultrafast molecular dynamics in time domain, because the femtosecond laser pulses required for resolving these dynamics necessarily have broad bandwidth, which prevents high-resolution spectroscopic measurements, transient absorption [9] [10] and time-resolved photoelectron spectroscopy [11] have been successfully applied to characterize the time-dependent electronic structure in numerous photo-induced reactions. Diffraction-based approaches such as X-ray scattering or electron diffraction, which yield high-resolution data on atomic positions, also have been recently adapted to ultrafast gas-phase studies. This became possible with a parallel development of X-ray Free-Electron Lasers (XFELs), which generate intense and ultrashort X-ray pulses (from tens of fs down to sub-fs regime) [12] and ultrafast electron sources capable of delivering femtosecond electron bunches [13] [14]. In addition, complementary approaches utilizing molecules’ own ionized electrons to image itself, such as laser-induced electron diffraction (LIED) [15] [16] or inner-shell photoelectron diffraction [17], have recently shown potential to achieve sub-Angström spatial and few-fs temporal resolution.

Despite the power of novel ultrafast techniques briefly discussed above, direct imaging of the motion of individual atoms in photo-induced reactions still remains challenging. It often heavily relies on the availability of elaborated theoretical modelling, including electronic structure calculations for the states involved in the reaction, which is typically challenging in itself. In addition, in most of the cases an imaging experiment focuses on a dominant pathway of a reaction. If there are several contributing pathways, disentangling them represents another major challenge. Finally, the most direct time-resolved methods for molecular structure determination in a gas phase, such as ultrafast electron diffraction (UED) or ultrafast

X-ray diffraction (XRD), deal with a large ensemble of molecules. These methods average all possible molecular orientations or requiring an additional laser pulse for molecular alignment [18].

A complementary imaging technique that allows one to address some of the challenges outlined above is the so-called Coulomb explosion imaging (CEI) [19] [20]. In CEI, a molecule is rapidly ionized, losing two or more electrons, and undergoes rapid dissociation (“explosion”) due to the Coulomb repulsion between the positively charged nuclei. The information on molecular geometry is then obtained from the measured kinetic energies, emission angles or momenta of the created ionic fragments. If multiple ionizations can be made nearly instantaneous, independent of the initial geometry, and the molecule is charged highly enough, such that the potential energy surfaces (PES) in the final state approach purely Coulombic ones, this information can, in principle, be obtained without a priori knowledge of the electronic structure of the initial state. These conditions were to a large extent realized in the early CEI experiments employing collisions of fast molecular ion beams with thin metal foils to strip most of the electrons [19]. However, as a price for its direct sensitivity to nuclei positions, the CEI technique provides essentially no information on the initial electronic state of the molecule.

For a time-resolved measurement, the CEI technique is normally combined with a standard two-pulse “pump-probe” scheme, where the first pulse (the “pump”) initiates molecular dynamics of interest, and the second synchronized pulse (the “probe”), arriving at variable time delay, monitors the temporal evolution of the system via CEI. Even though the ideal conditions outlined above are seldom completely fulfilled in light-induced CEI, it has been successfully applied to distinguish geometrical [21] or conformational [22] isomers, to probe vibrational motion in diatomic [23] and simple polyatomic [24] molecules, to visualize molecular dissociation, and to characterize rotational wave packets produced by laser alignment [25]. It has also been employed to study more complicated photo-induced reactions like isomerization in simple hydrocarbons [26] [27], hydrogen migrations in alcohols [28] [29], and, very recently, roaming reactions [30]. While the reconstruction of (unknown) molecular geometry based solely on the CEI experimental data is still out of reach, this approach, espe-

cially in the coincidence mode, yields a comprehensive set of kinematical constraints, which allows one to discriminate between different geometries and reaction scenarios and can often benchmark theoretical predictions.

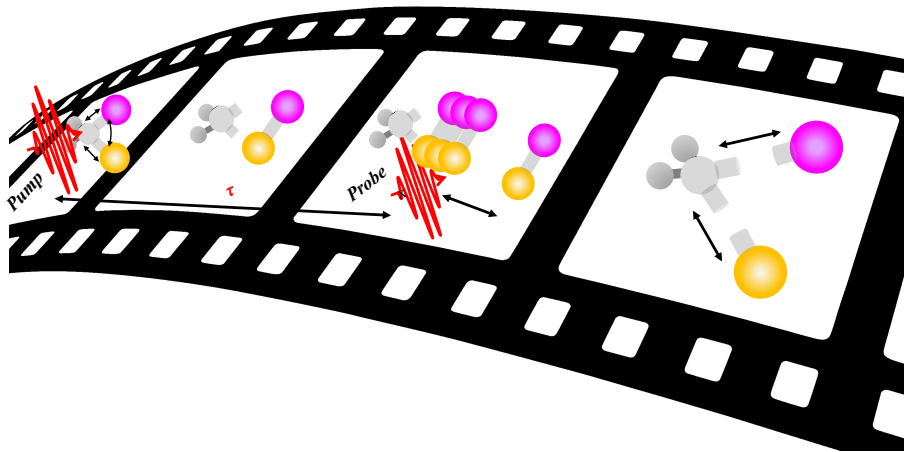


Figure 1.1: Cartoon illustrating the pump-probe scheme in a molecular system for imaging the transient geometries of various dissociation channels. Here, the pump pulse triggers dissociation and the fragments separate with an increase in delay. Later on, at each delay (τ), the probe pulse fragments the dissociating molecule and leading to a three-body breakup.

The main objective of this work is to apply time-resolved CEI technique to study breaking and formation of chemical bonds in three laser-irradiated halomethane molecules (CH_2I_2 , CH_2ICl , CH_3I). Halomethanes (halogen-substituted methanes) represent attractive and popular model systems for studying prototypical photochemical events and for the development of novel schemes for laser-controlled chemistry [31] [32] [33]. The studies described in this thesis cover three different regimes of light-molecule interactions: (1) dynamics induced by an intense near-infrared (NIR) field, mainly unfolding on low-lying cationic states; (2) dynamics in the excited states of a neutral molecule driven by ultraviolet (UV) light; and (3) cationic dynamics triggered by photoionization by a single extreme ultraviolet (XUV) photon. We specifically focus on several aspects of halomethane photochemistry that are of general importance, have been actively discussed in literature, and yet are difficult to access using established imaging or spectroscopic techniques discussed above. In particular, this includes mapping of transient isomer formation, visualizing different pathways leading to the molecular halogen elimination and disentangling two-body and three-body dissociation

channels. While the picosecond-scale isomerization of diiodomethane (CH_2I_2) was clearly demonstrated in solution, and was recently shown to occur due to the interaction with solvent [34], the existence of a much faster, intra-molecular pathway was suggested for the gas phase [35] [36]. Here, we provide direct evidence of ultrafast, sub-100 fs CH_2I_2 isomerization, and demonstrate that the decay of the short-lived isomer opens up an additional pathway for molecular iodine elimination.

The experiments described in this thesis have been performed employing optical lasers at James R. Macdonald Laboratory (JRML) at Kansas State University, and at the Free-electron LASer in Hamburg (FLASH) at Deutsches Elektronen-Synchrotron (DESY) facility in Germany. The document is organized as follows: Chapter 2 begins with several introductory concepts important for understanding different regimes of light-induced dynamics in polyatomic molecules, provides a brief (and incomplete) overview of relevant earlier studies on halomethanes, and briefly describes modelling tools used in this work. Chapter 3 contains an overview of experimental tools used here, including a brief description of a laser system used to generate femtosecond NIR and UV pulses at the JRML, an overview of FLASH-II free-electron laser (FEL) facility and XUV-pump XUV-probe arrangement, as well as charged-particle imaging spectrometers used in both laboratories. Chapter 4 is devoted to the studies of strong-field-induced dynamics in two di-halomethane molecules, CH_2I_2 and CH_2ICl . It starts with the results of single NIR pulse measurements (at 800 nm), discussion of different ionization channels, and identification of the contribution from concerted and sequential molecular breakup mechanisms. Then we describe a series of pump-probe experiments employing one NIR pulse as a pump, and a second, more intense pulse of the same color as a probe. This section focuses on the characterization of different vibrational modes excited by the NIR pump pulse via channel- and energy-resolved Fourier spectroscopy, on the identification of different dissociation pathways, and on the experimental separation of the molecular halogen elimination (I_2 or ICl for di-iodomethane and chloro-iodomethane, respectively). In Chapter 5, the results of the UV-pump (266 nm) and NIR probe experiments on di-iodomethane are presented. This chapter focuses on the characterization of the transient $\text{CH}_2\text{I-I}$ isomer, its formation and decay times, I_2 elimination from the initial molecular

configuration and from the isomer, and on disentangling two- and three-body dissociation channels. The latter mechanism, which can be easily separated using our experimental approach, is notoriously difficult to identify with most of the other techniques. Chapter 6 describes XUV-pump – XUV probe experiment (wavelength 52.8 nm, photon energy 23.5 eV) on CH_2ICl and CH_3I molecules at FLASH FEL facility. Here, the main focus is on the discussion of the electron transfer between the two sites of a dissociating molecular ion, and its dependence on the internuclear separation. Finally, Conclusions and Outlook are presented in Chapter 7.

Chapter 2

Basic photo-induced processes in halomethanes

2.1 Introductory considerations

A molecule is a combination of two or more atoms bound together. When multi-electron atoms associate to form molecules, the distribution of the tightly bound inner shells of electrons (“core-shells”) remains largely undisturbed and localized around their nuclei, and the binding forces are provided by the distribution of outer (“valence”) electrons, that are distributed across the molecule [37]. Since the electronic motion in molecules is typically much faster than the motion of the nuclei, the electronic and nuclear motion can be essentially treated independently, and the electronic states can to a good approximation be determined for a specific, fixed set of nuclei positions – the approach known as the Born-Oppenheimer (BO) approximation” [38]. Such separation can allow for an analytic solution of the Schrödinger equation for a nuclear wave function of many-electron, many-nuclei system. Although the BO approximation fails to describe some important physical and chemical phenomena, in particular, in photochemistry [39], it provides very useful and intuitive framework for understanding molecular phenomena, and, in particular, molecular response to light. Within the BO approximation, it can be rationalized in terms of potential energy surfaces

(PES) calculated for each electronic state as a function of the geometry of the nuclei.

A molecule irradiated with light can absorb one or more photons, depending on the wavelength and the intensity of light. This can result in the excitation of the molecule to a higher-energy state, or in the ejection of one or more electrons – the process usually referred to as “ionization”, or “photoionization”. Both excitation and ionization can also result in a significant change of molecular geometry. An important and frequent example of a drastic geometry change is the so-called photodissociation, where an interaction with light results in breaking one or several molecular bonds. However, in many cases photoabsorption or ionization can cause a significant bond rearrangement or a formation of new bond(s), while the molecule remains bound. In terms of the PESs, a photo-induced reaction following excitation from the molecular ground state can be perceived as a classical trajectory or a wave packet propagating on the excited-state (or ionic) PES. This is often accompanied by a significant vibrational and rotational excitation.

If the incident light field is weak enough, such that the probability to absorb more than one photon is negligible, the photoabsorption spectrum and the molecular response are governed by the relation between the photon energy and the structure of molecular PES. In this case, ionization can occur if the photon energy is larger than the binding energy of an electron (“ionization potential, I_p ”). Whether a given light field can be considered “weak” in this sense, depends on the parameters of the field (mainly, its wavelength and intensity), and on the photoabsorption cross section at this wavelength. For any given wavelength, above certain intensity value, two- and multiphoton absorption processes become non-negligible. This significantly broadens a range of accessible bound and continuum states. In particular, this opens up a possibility of multiphoton ionization at the photon energies below the ionization potential of the molecule.

As sketched in Fig. 2.1, at high intensities and rather small photon energies (low-frequency field), the ionization process can be more efficiently understood in terms of the electron tunneling out through the potential barrier lowered by the slowly-oscillating laser field. The transition between multiphoton and tunneling regimes of ionization can be characterized by the so-called Keldysh, or adiabaticity parameter γ , which is determined by the

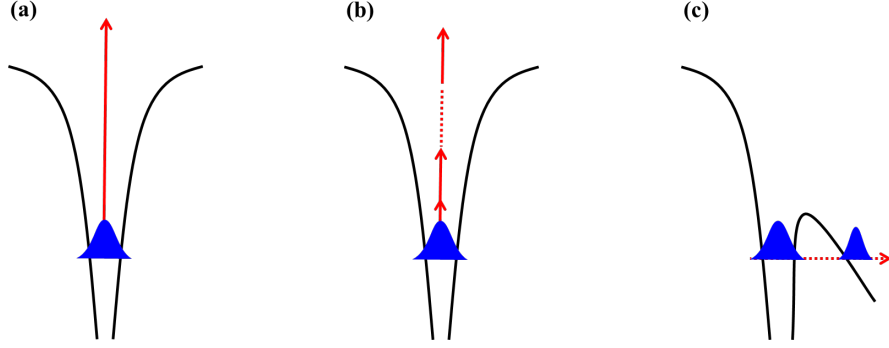


Figure 2.1: Ionization scenarios in the strong-field regimes: (a) single ionization, (b) multi-photon ionization, (c) tunneling ionization

ratio of time required for the electron to tunnel out ($T_{tunneling}$) to the laser time period (T_{laser}), and is given by

$$\gamma = \sqrt{\frac{I_p}{2U_p}} \propto \frac{T_{tunneling}}{T_{laser}} \quad (2.1)$$

where $U_p[eV] = 9.34 \times 10^{-20} \times (\lambda[nm])^2 I[w/cm^2]$

is the so-called ponderomotive potential, i.e., the wiggling energy of a free electron oscillating in a light field of wavelength γ and intensity I . If $\gamma > 1$, the ionization can be considered as a multi-photon process. In this regime, the low-order perturbation theory suggests that the rate of n -photon absorption is proportional to I^n . $\gamma < 1$ corresponds to the regime of tunneling ionization, where the ionization rate depends on the intensity exponentially as,

$$w_{tunnel} \propto \exp \left[-\frac{2}{3} \frac{I_p}{\sqrt{I}} \sqrt{2I_p} \right] \quad (2.2)$$

and the motion of the emitted electron in the continuum can be to a good approximation considered as a classical motion in a combined optical field and the field of the remaining ion [40]. This parameter range is often referred to as “strong field” regime. At even higher field intensities, the Coulomb potential can be completely suppressed by the oscillating laser field, and the ionization can occur via “over-the-barrier ionization (OBI)” mechanism.

The work presented here covers all of the regimes of light-molecule interactions discussed above: single-photon UV excitation of a neutral molecule; few-photon ionization by the

UV light, as well as NIR “strong field” single and multiple ionization in the tunneling and OBI limit. Moreover, in Chapter 6, we address the dynamics induced by single-photon ionization at XUV wavelengths. Correspondingly, the next three sections describe basic relevant molecular phenomena for each of these regimes, with the focus on specific family of molecules, halomethanes.

2.2 Photoprocesses triggered by a single UV photon

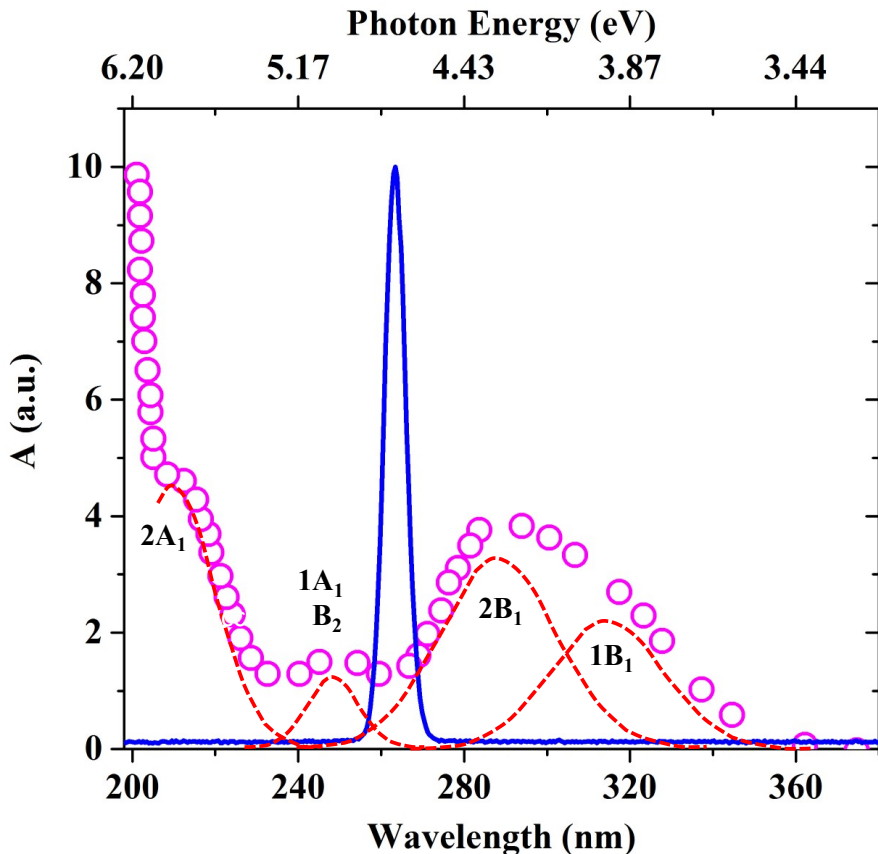


Figure 2.2: UV absorption spectrum for CH_2I_2 molecule along with the UV pulse spectrum. Dashed regions are the gaussian bands to low-lying electronic states (adapted from [41])

When a photon of ultraviolet (UV) light is absorbed by a molecule, it undergoes a transition to one of its higher-lying states. While the typical UV photon energies of a few eV are below the first excited level in isolated atoms, they can be very efficiently absorbed in molecular systems. In contrast to narrow atomic lines, polyatomic molecules exhibit broad

absorption bands, which often overlap and becomes more and more complicated in larger systems. For example, an iodomethane molecule (CH_3I), the prototypical system for studies of UV-driven photochemistry [42], manifest essentially a single broad band centered around 260 nm. In contrast, already di-halomethanes, with one more hydrogen atom replaced by a halogen, exhibit a much richer absorption spectrum. An example of such spectrum is shown in Fig. 2.2 for diiodomethane (CH_2I_2). Its main features are currently well-understood based on many experimental and theoretical studies [43] [41] [44] [45]. The spectrum is typically deconvoluted into four broad bands centered at 312, 288, 249, and 212 nm [44] [45]. These four bands reflect transitions from the electronic ground state (X^1A_1) to several low-lying electronic states sketched in Fig. 2.3. Although the maximum of the overall absorption spectrum lies close to 300 nm, at those wavelengths only the lowest excited states can be reached. The photoabsorption at ~ 266 nm – the wavelength used in this work – results in the population of somewhat higher-lying states.

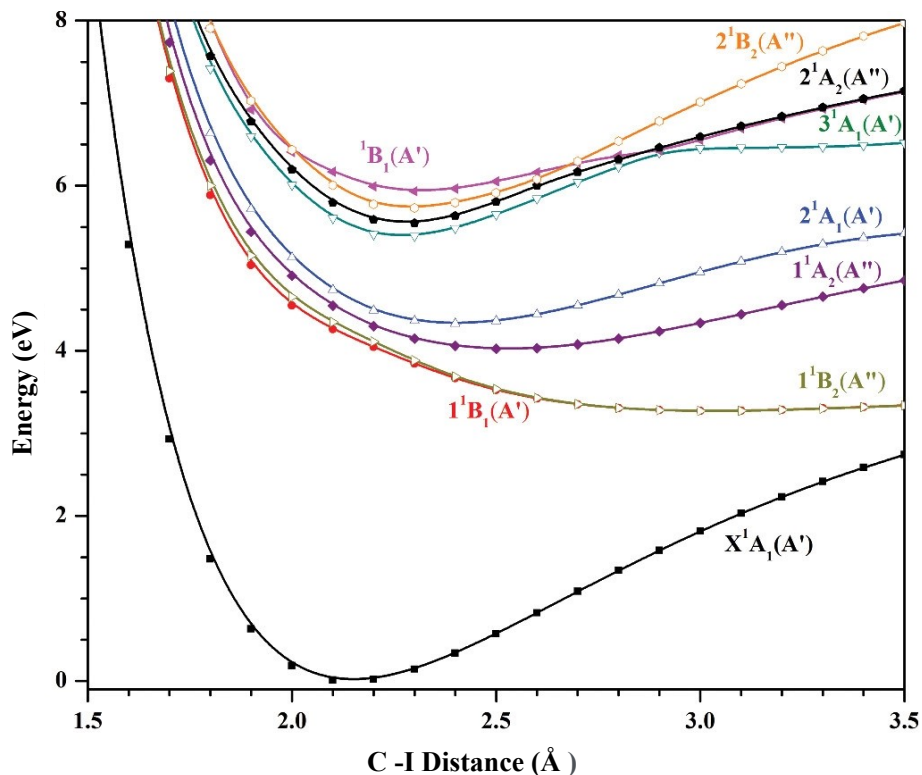


Figure 2.3: A cut through the calculated CH_2I_2 potential surfaces along the C-I distance in the Franck-Condon region showing low-lying electronic states responsible for the absorption spectrum of Fig. 2.2 (from [45]).

Major photodissociation channels

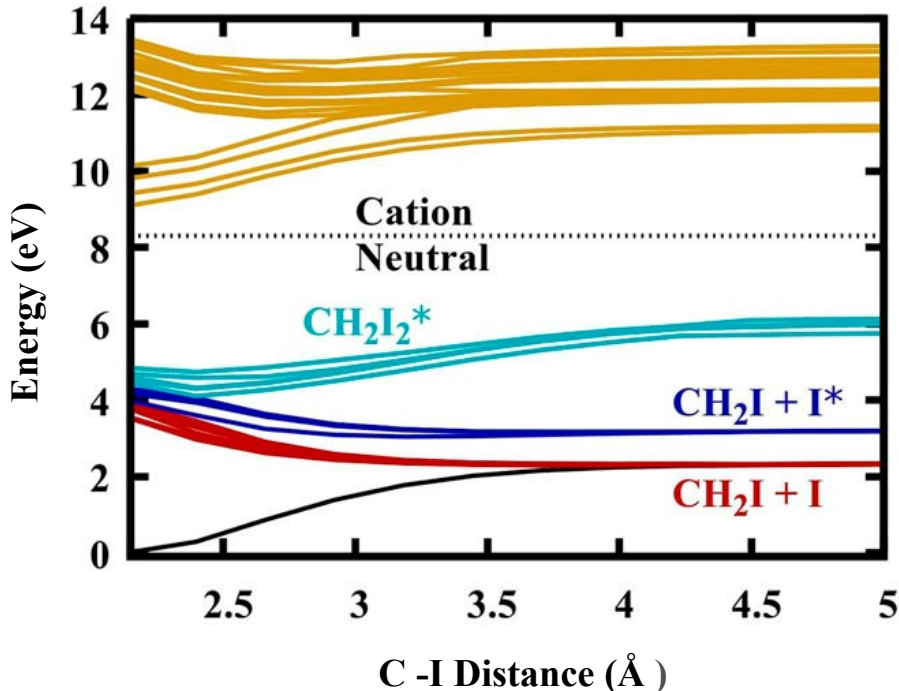


Figure 2.4: Potential energy as a function of C-I distance for several neutral and cationic CH_2I_2 states in the outer region illustrating dominant dissociation pathways (from [46]).

When a halomethane molecule breaks up upon UV photoabsorption, the dominating dissociation channels normally result from a cleavage of one or more carbon-halogen bond. For the example of diiodomethane considered above, two major dissociation processes are (1) $\text{CH}_2\text{I}_2 \rightarrow \text{CH}_2\text{I} + \text{I}^* \text{ } ^2P_{1/2}$ and (2) $\text{CH}_2\text{I}_2 \rightarrow \text{CH}_2\text{I} + \text{I} \text{ } ^2P_{3/2}$, which originate from the breaking of one of the C-I bonds and results in the production of excited- and ground-state iodine atoms, respectively. This pair of spin-orbit split channels is very typical for the photodissociation of halomethanes with one or more iodine atoms [47]. The path towards these dissociation channels is illustrated in Fig. 2.4, which shows the schematics of the diiodomethane potential energy curves in the outer region. These two channels have been extensively characterized using spectroscopic methods [48], time-resolved photoelectron spectroscopy [46], ion imaging [49] and ultrafast electron diffraction (UED). Earlier studies [44] showed that at 266 nm, pathway (1) resulting in the production of $\text{I}^* \text{ } ^2P_{1/2}$ fragments is the dominant one. Recent experimental and theoretical analysis of photoelectron, photoion

and UED data suggests that the main photodissociation mechanisms at 266 nm are driven by the initial population of the bound excited states (cyan lines in Fig. 2.4) and subsequent internal conversion to the lower repulsive curves, which occurs via two different pathways, either directly or with $\sim 150 - 200$ fs delay [50]. The final population of the higher repulsive state (channel (1), $\text{CH}_2\text{I} + \text{I}^*$, blue curves in Fig. 2.4) is about a factor of 3.75 higher than the lower one (channel (2), $\text{CH}_2\text{I} + \text{I}$, red curves) [49].

Three-body dissociation and molecular halogen elimination

Besides two major pathways, the other dissociation channels that are discussed in literature and are relevant for this work are (3) three-body dissociation $\text{CH}_2\text{I}_2 \rightarrow \text{CH}_2 + \text{I} + \text{I}$; and (4) ejection of molecular iodine $\text{CH}_2\text{I}_2 \rightarrow \text{CH}_2 + \text{I}_2$ – the reaction often referred to as “ I_2 elimination”. Both of these channels require breaking of the two C-I bonds, whereas the latter channel also involve a new I-I bond formation. On the basis of thermochemical data, it was suggested that a threshold wavelength for the three-body dissociation lies at 245 nm [44] or 250 nm [51], corresponding to photon energies of ~ 5 eV. However, to the best of our knowledge, no experimental data on three-body neutral dissociation of diiodomethane have been reported, even though it was suggested to play a role in UV-induced fragmentation of other halomethanes following two-photon absorption [52]. Overall, a clear identification of the three-body breakup of neutral molecules and its separation from other dissociation channels typically represents a severe experimental challenge [53] [54] [55].

The energetic threshold for molecular halogen elimination is typically somewhat lower. In diiodomethane, the energy needed to eject I_2 is estimated to be 4.04 eV (307 nm). Correspondingly, I_2 elimination driven by a single-photon absorption in the UV domain has been reported for CH_2I_2 as well as for other halomethanes [51] [47]. It was also extensively discussed in a series of early femtochemistry papers by M. Dantus’s group, where it was triggered by two- or few-photon absorption [56] [57]. Such molecular halogen elimination was discussed in terms of different mechanisms illustrated in Fig. 2.5. While different concerted pathways can readily occur in gas-phase molecules, the stepwise, or “sequential” mecha-

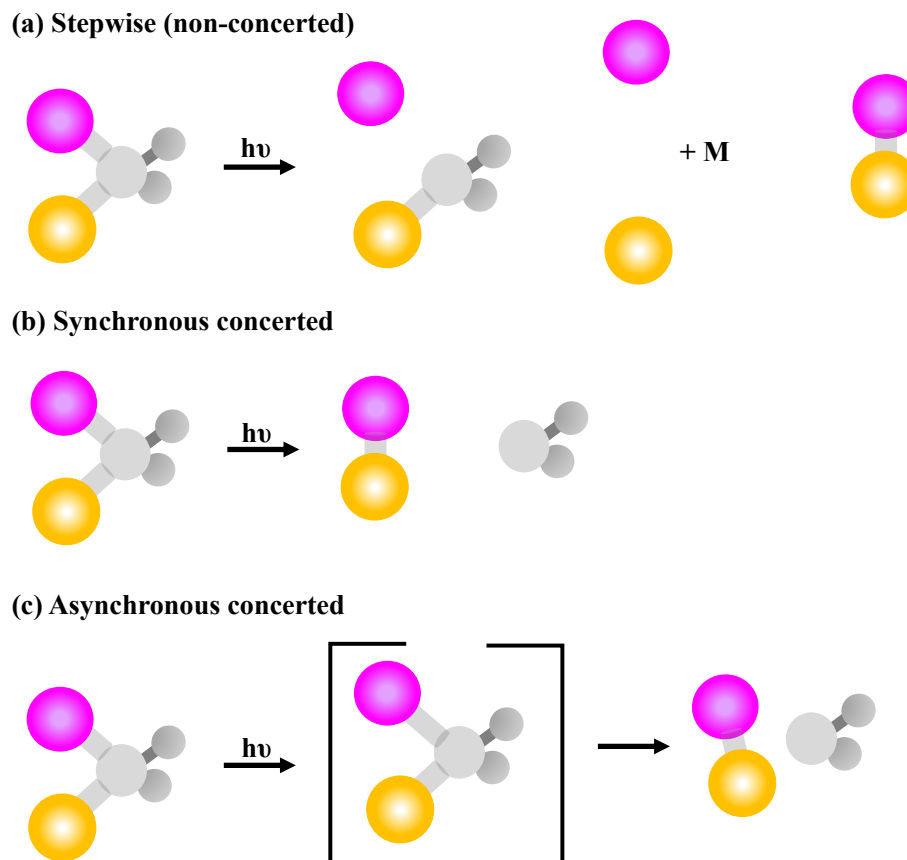


Figure 2.5: Possible mechanisms of molecular halogen elimination (adapted from [56]).

nism for the diatomic formation requires a collision with a third body, which could, e.g., be represented by a solvent molecule [58].

Photoisomerization

Besides photodissociation, upon photoabsorption, a molecule can undergo significant structural changes, while remaining bound. An important class of such transformations is known as isomerization, i.e., an interconversion between different isomers, which are identical in chemical composition but different in molecular geometry. Isomerization reactions range from simplest prototypical example, a transformation between acetylene (HCCH) and vinylidene (H_2CC), to very complicated reactions in large molecular systems like those responsible for the primary step in vision [59]. Isomerization can be reversible if the molecule periodically “flips” between two different geometries, “permanent”, if the product isomer remains

stable, and, finally, transient, if the isomer decays after a certain time. It can be also a purely intramolecular effect, or it can originate from intermolecular interactions, in particular, from collisions with solvent molecules.

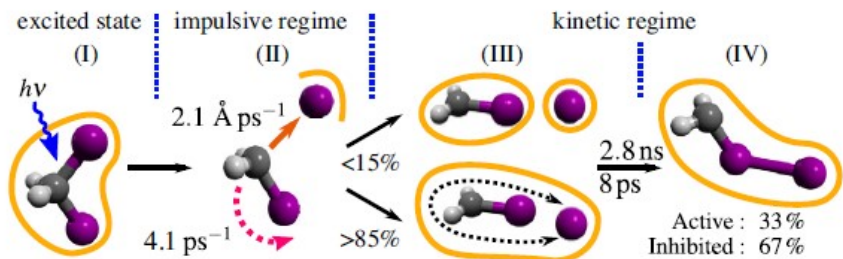


Figure 2.6: CH_2I_2 isomerization in solution (from [34]).

For halomethanes, the solvent-mediated isomerization occurring on ps time scale is considered to be a well-established mechanism. In an oversimplified picture (see Fig. 2.5), absorption of light (e.g., at 266 nm) results in fast C-I bond cleavage, yielding CH_2I and I fragments, which, in contrast to the case of an isolated molecule, are confined by the solvent molecules. Within picoseconds, the fragments are forced to recombine to form a photoisomer, $\text{CH}_2\text{I-I}$, with the efficiency ranging from 70 to 85 % [34] [58]. On nano- and microsecond timescales, the isomer and radical pair fragments undergo further intermolecular reactions, forming I_2 and partially reforming the parent molecule [60]. However, recent calculations suggest that a much faster, sub-100 fs intramolecular isomerization occurs in the isolated CH_2I_2 molecules [36] [35]. The simulated pathway towards fast isomer formation is illustrated in Fig. 2.7. The created isomer supposedly decays within a few hundred femtoseconds, ejecting either a single iodine atom or molecular I_2 [35]. Although a dedicated time-resolved transient absorption measurement [36] provided some evidence supporting the existence of such short-lived transient isomer, this finding is still debated [34]. The experimental verification of the existence of such transient structure, and determination of its formation and decay times is one of the main objectives of this work.

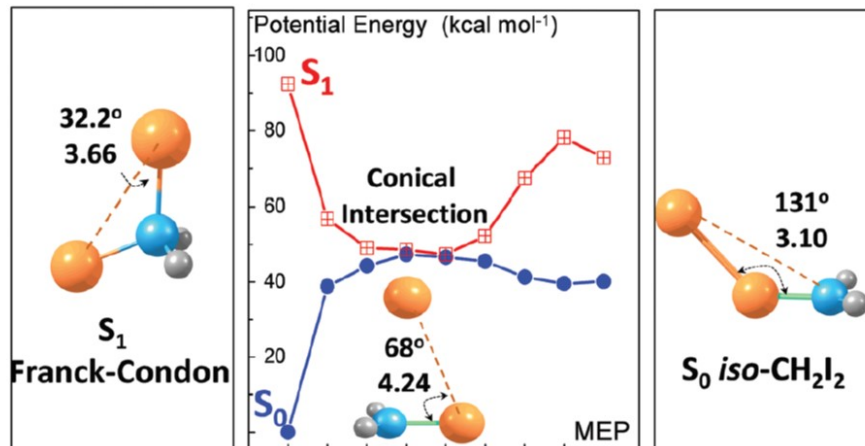


Figure 2.7: Calculated path to short-lived isomer formation (from [36]).

Processes driven by two- or few-photon absorption

The UV spectrum used in this work is centered at 263.5 nm (4.71 eV), with a bandwidth of ~ 7 nm. The vertical ionization potential of CH_2I_2 molecule is 9.46 eV. Correspondingly, the absorption of the two photons leaves the molecule either slightly below or slightly above the ionization threshold, populating either the high-lying Rydberg states or the lowest cationic states. The shapes of the potential energy surfaces for the Rydberg and ionic states are very similar since they are both determined by the removal of a HOMO (iodine lone pair) electron, which leads to significant displacement along the I-C-I bending coordinate [50] [61].

As can be seen from Table 2.1, which shows the experimentally measured energy threshold for the appearance of various fragment ions [62], two-body dissociative ionization pathways resulting in $\text{CH}_2\text{I} + \text{I}^+$, $\text{CH}_2\text{I}^+ + \text{I}$ and $\text{CH}_2 + \text{I}_2^+$ (I_2^+ elimination) would require the absorption of at least three photons. The neutral I_2 elimination ($\text{CH}_2^+ + \text{I}_2$) or the three-body dissociation channel $\text{CH}_2^+ + \text{I} + \text{I}$ in the ionic state would require at least four UV photons to be absorbed.

Dissociation Pathways	Appearance energies (eV)
CH_2I_2^+	9.46
$\text{CH}_2\text{I}^+ + \text{I}$	10.55
$\text{CH}_2 + \text{I}_2^+$	12.76
$\text{CH}_2\text{I} + \text{I}^+$	13.20
$\text{CH}_2^+ + \text{I}_2$	13.80
$\text{CH}_2^+ + \text{I} + \text{I}$	15.40

Table 2.1: Appearance energies for different dissociation products from the singly-charge diiodomethane [62].

2.3 Multiphoton and strong-field driven dynamics

When an atom or a molecule is exposed to an external laser field of high enough intensity, it can be efficiently ionized even if the laser photon energy is well below the ionization potential. As discussed in the first section of this Chapter, depending on the laser parameters (or, more specifically, on the value of the Keldysh parameter γ), the ionization can be considered as a multiphoton or a tunneling process. However, for many practical situations γ is rather close to 1, and the choice between “the photon” and “the field” picture becomes more a matter of convenience and language, and largely depends on the requirement of a specific application. Many important “strong-field” phenomena such as above-threshold ionization (ATI), high-order harmonic generation (HHG) and non-sequential double ionization (NSDI) often occur in this regime. For molecules, intense laser pulses enable novel imaging schemes like HHG-spectroscopy [63], laser-induced electron diffraction (LIED) [16], channel-resolved ATI [64] and laser-induced Coulomb explosion [30], which is the tool of choice for this work. Understanding strong-field dynamics is thus important for developing and refining these applications. Moreover, strong, low-frequency laser fields provide experimental tools capable of modifying the potential surfaces of molecules, paving the way towards optical control of molecular reactions.

In most of the cases discussed above, laser fields with the wavelengths of ~ 800 nm or longer, are employed, such that single-photon transitions from the ground to an excited electronic state of the neutral molecule are out of reach. Most typical phenomena thus

include either a (multiphoton) excitation to a high-lying state, or ionization, such that most of the dynamics occur in the highly excited or ionic states. Besides that, a typical effect of a strong laser pulse on a neutral molecule is its rotational excitation in the electronic ground state, which occurs via Raman-type transitions and can be efficiently exploited for molecular alignment [65]. Raman processes can also excite low-lying vibrational modes in the electronic ground state of the molecule if the laser bandwidth is large enough to cover the energy difference to the ground vibrational level [23] [66].

Single ionization, cationic vibrational dynamics and dissociative ionization

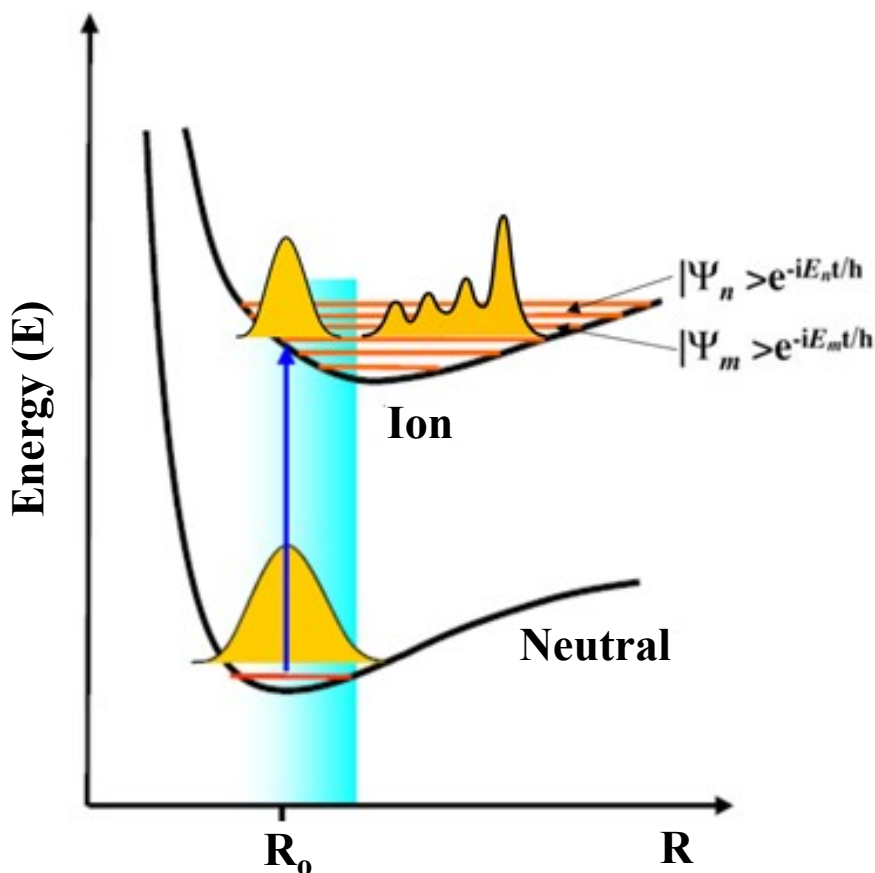


Figure 2.8: A cartoon illustrating the creation of the ionic vibrational wave packet by ionization of a diatomic molecule.

On top of atomic effects, ionization of molecules depends, in general, on its geometry and spatial orientation. According to the Franck-Condon principle, ionization can be represented

as a vertical transition from a point on the lower-state PES to the same nuclear configuration on an upper (in this case, cationic) surface, relying on the BO picture outlined in Section 2.1 [37]. Correspondingly, the resulting vibrational state distribution of the ion and ensuing dynamics strongly depend on the relation between the neutral and cationic state geometries. For diatomic molecules, it is determined by the difference in the equilibrium distances. If the ionizing pulse is short compared to the vibrational period, it creates a coherent superposition of ionic vibrational states – a vibrational wave packet with the well-defined phase. As sketched in Fig. 2.8, if the ionic equilibrium distance is larger than that of the neutral, the created wave initially propagates outwards. Within a pump-probe scheme, such wave packet can be probed by projecting it to one of the higher-lying states. The resulting time-dependent signal contains the time-dependent modulation frequencies, $(E_n - E_m)/\hbar$, which correspond to the set of level spacings in the coherent superposition. Its Fourier transform yields the corresponding frequencies, which, depending on a particular probe scheme, can be channel-, energy- or angle-resolved [67].

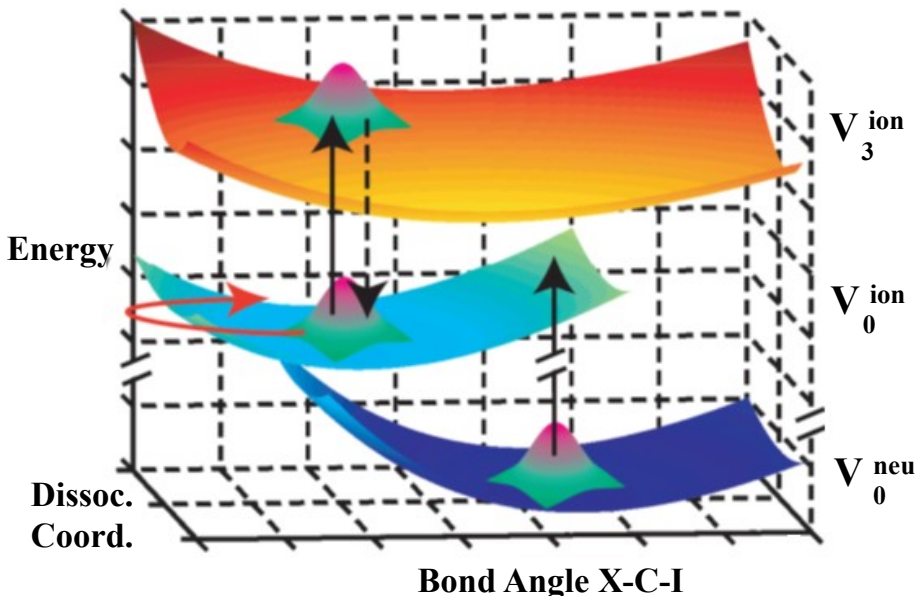


Figure 2.9: A cartoon of the CH_2XI ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) potential surfaces for ionic and neutral ground states, and for one of the ionic excited states, illustrating the displacement of the ionic ground state along the angular coordinate (from [68]).

For polyatomic molecules, vibrational dynamics upon ionization can be much more com-

plex, and the created wave packets in general can contain multiple vibrational modes. For halomethanes with a single halogen atom, like CH_3I , the ionic vibrational motion is still often dominated by a single vibrational mode, stretching along carbon-halogen bond [24] [66]. For di-halomethanes, the ionic nuclear configuration is displaced along the angular coordinate, resulting in large-scale bending vibrations upon ionization, as shown in Fig. 2.9. Fig. 2.10 schematically depicts basic relevant vibrational modes for diiodomethane.

Earlier single-color pump-probe experiments on diiodomethane in strong-field regime employing ion mass spectrometry as a probe, revealed that both, parent ion and fragment ion yields are sensitive to the I-C-I bending vibrations (the so-called “scissors mode”) [69], [70]. Very recent transient absorption experiment [71] demonstrated that in addition to this, symmetric stretching vibration is also excited upon strong-field ionization.

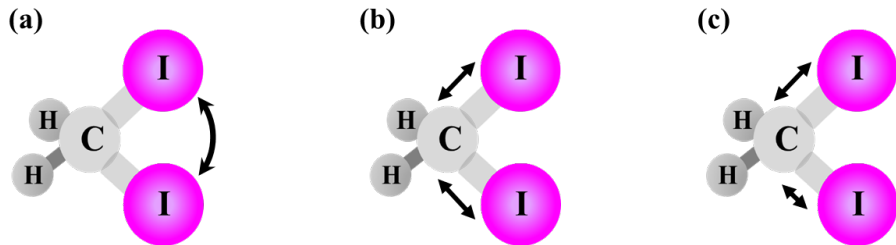


Figure 2.10: Sketch of vibrational modes in CH_2I_2 molecule: (a) I-C-I bending mode (b) C-I symmetric stretching mode, and (c) C-I asymmetric stretching mode

Dissociative ionization and ionic resonances

The dissociation of molecular ions can proceed via direct ionization to one of the repulsive or predissociative states, or via initial population of a bound or metastable states and subsequent internal conversion to the repulsive curve. However, for intense NIR or mid-IR wavelengths a typical scenario is the initial population of one of the low-lying bound states, and subsequent one- or few-photon transition to a repulsive or predissociative curve. Generally, there are multiple ionic states available, since there are multiple electron orbitals. The energies associated with ionizing from many of these orbitals may be quite similar, and the corresponding ionic states can be readily coupled with one NIR photon [68] [69] [70]. Furthermore, since the equilibrium geometry of the ion is generally different than that of the

neutral molecule, ionization produces large amplitude vibrational motion in the ion which makes such ionic resonant transitions inherently dynamic [68] [69]. For pulses longer than the corresponding vibrational period, the wave packet will pass all resonant geometries while the field is still on. While this is not necessarily the case for pulses shorter than the vibrational period, such resonant transitions can be induced by adding a probe pulse of the same color.

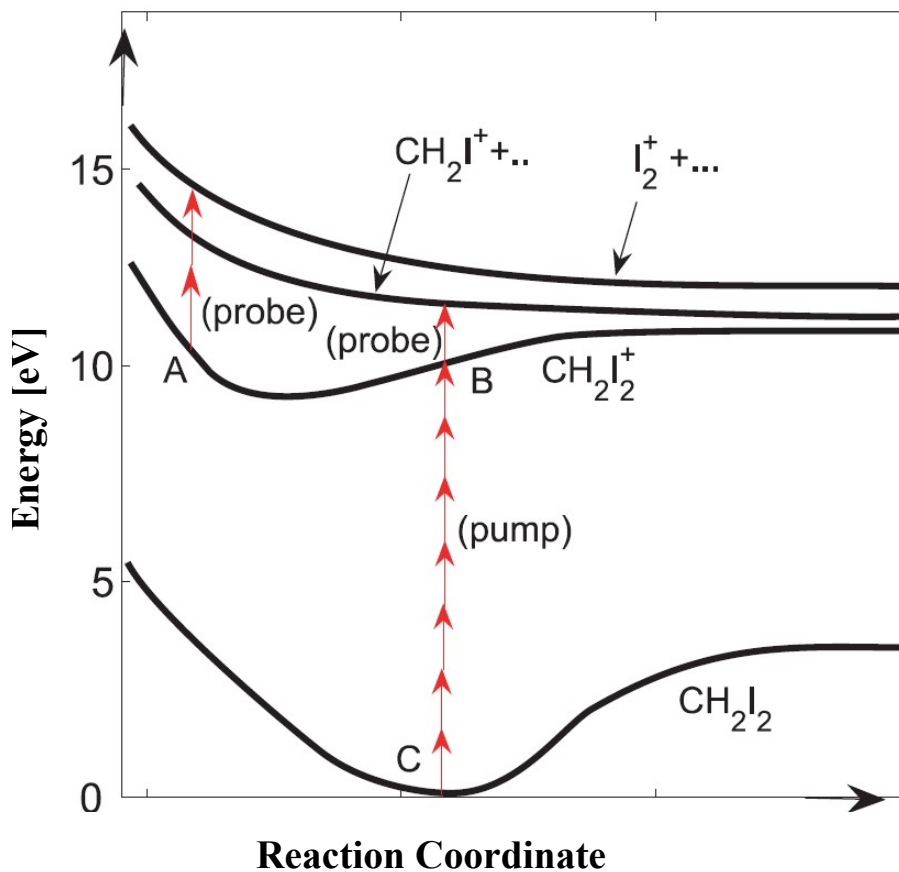


Figure 2.11: A cartoon of potential energy curves with respect to the angular coordinate in diiodomethane illustrating the suggested relation between the bending vibrational motion and two different dissociation channels (from [69]).

The relation between the cationic bending vibrations, transient resonances and dissociation pathways derived in [69] is illustrated in Fig. 2.11 for two-pulse dissociative ionization of diiodomethane. Here, the wave packet starting at a point A on the neutral ground state, is transferred to the point B on the ionic ground state by vertical ionization induced by the pump pulse. The created ionic wave packet propagates towards the equilibrium geometry

of the ionic state, i.e., to smaller angles. Near the Franck-Condon region, it can undergo a single-photon transition to one of the higher-lying states, resulting in the dissociation of a molecular ion via $\text{CH}_2\text{I}^+ + \text{I}$ channel. At the inner turning point, where the I-C-I angle and, thus, the I-I distance is the smallest, a two-photon transition induced by the probe can result in I_2^+ elimination from the cation [69] [70].

The main objective of the strong-field part of this work is to shed light on the relation between different dissociative ionization pathways and the vibrational wave packet motion, to characterize the time-dependent nuclear geometry for I_2^+ (or I_2) elimination, and, last but not least, to develop and test the laser-induced CEI as a probe of femtosecond nuclear dynamics in small polyatomic molecules.

Multiple ionization and fragmentation mechanisms

While in the last example considered above, the pump-probe scheme could work well with moderately intense pump and probe pulses and the (dissociating) final state of the molecule after the probe pulse was still singly charged, an efficient CEI probe should result in double or multiple ionization. In molecules, double and especially multiple ionization in most cases lead to a rapid dissociation yielding high energy fragments – hence the term “Coulomb explosion” (CE). This term is somewhat misleading for relatively low charge states, since di- and tri-cationic potential surfaces typically deviate from purely Coulombic ones at small internuclear separations. Many doubly- and even some triply-charged molecular ions exhibit bound or metastable states. They result in rather large deviations of the measured fragment energies from the values expected for pure CE and, in case of metastable states, result in significant complications in the interpretation of the CE data. The main problem here is that these states survive long after the laser pulse, but decay on their way to the detector, on the time scale longer than the characteristic molecular rotations [72]. The resulting ionic fragments that are identical to those from prompt, “concerted” molecular breakup in terms of their mass-to-charge ratio, do not carry any information about the molecular geometry at a time of the interaction with the laser pulse. Although data analysis methods allowing for

a reliable identification of such products in the coincident data have been recently developed [72] [73], they are in many cases still hindering effective implementation of CEI, or reducing its signal to noise ratio (see a more specific discussion in Chapter 4). Fortunately, these channels are essentially absent at large separations between the molecular nuclei, and also tend to disappear for higher charge states.

Mechanisms of double and multiple ionization by intense laser fields are usually classified into “direct”, or “non-sequential” and “sequential”, or “stepwise”. Here it should be noted that the term “sequential” applied to ionization is different from the same term in molecular fragmentation. In the latter case, “sequential” means a breakup mechanism, where one molecular bond is broken at a time, and a long-lived (with respect to its rotation) metastable intermediate decay at significantly later times, long after the pulse that initiated the breakup. In this case it is contrasted with “concerted” fragmentation. With respect to multiple laser ionization, the term “sequential” means a stepwise removal of atomic or molecular electrons, typically at different cycles of the oscillating optical field. In this case, it is contrasted with the so-called “direct” or “non-sequential” ionization. The dominant mechanism of the latter at NIR and mid-IR frequencies is electron recollision. Even though non-sequential, or recollision-induced ionization had been reported for a broad range of molecular systems and is often a dominant double ionization mechanism at moderate intensities, sequential multiple ionization at high intensities is clearly a preferred mechanism for CEI, because it can achieve higher charge states, and usually provide larger branching ratios when compared to single ionization. A rule of thumb to achieve sequential multiple ionization to n -fold charge state is to saturate the production of the $(n-1)$ state. For polyatomic molecules, where typical saturation intensities for single ionization can be reached at the intensity range from lower 10^{13} to lower 10^{14} W/cm², multiple ionization to triply, quadruply and five-fold charges can be readily achieved at the intensities well below 10^{15} W/cm², and the practical limits for intensity are set by background signals, and by the necessity to maintain low event rate needed for coincident CEI.

2.4 XUV-induced ionization, dissociative ionization and electron transfer

Besides serving as model polyatomic systems for UV-driven photochemistry and strong-field studies, halomethanes have recently become popular targets for free-electron laser (FEL) research. The main reason for this is their relative simplicity, well-studied photochemistry and the presence of a heavy halogen atom, which provides a variety of absorption edges with large absorption cross section available for inner-shell studies. Recent XUV and X-ray experiments mainly focused on iodomethane (CH_3I) molecules [74] [75] [76] [77] [78], [79] [80] [52] [81], although di-halomethanes have also been studied [82] [83] [84] [85] [86]. Besides studying the fundamentals of light-molecule interaction in a new XFEL regime [75] [78], these experiments largely focused on investigating electron transfer (ET) processes in dissociating molecules. The availability of short X-ray pulses enabled localized inner-shell photoionization in conjunction with a synchronized optical laser, thus allowing for time-resolved studies. In many pump-probe experiments [74] [77] [79] [80] [81], it was exploited to create a localized charge on one site of a laser-dissociated molecule, and to study the ET probability as a function of internuclear separation.

A concept of such experiment is sketched in Fig. 2.12 (a). Here, a pump pulse dissociates the molecule, and the X-ray probe pulse ionizes one of the inner-shells of the detached halogen atom. Depending on the delay between the two pulses, internuclear separation, and, thus, the ET probability varies, becoming rather unlikely or essentially forbidden at large distances. As an observable for such distance-dependent probability, it was suggested [74] to exploit the appearance of low-energy highly charged halogen ions, which essentially monitor the probability of a partner fragment (e.g., a methyl group in CH_3I) to remain neutral. An outcome of such experiment described in Ref. [74] is illustrated in Fig. 2.12 (b). The measured yield of low-energy highly-charged iodine ions created by X-ray ionization of iodine 3d shell in laser-dissociated CH_3I is plotted as a function of laser-X-ray delay, which is recalculated into the internuclear separation. These curves reflect the probabilities for CH_3

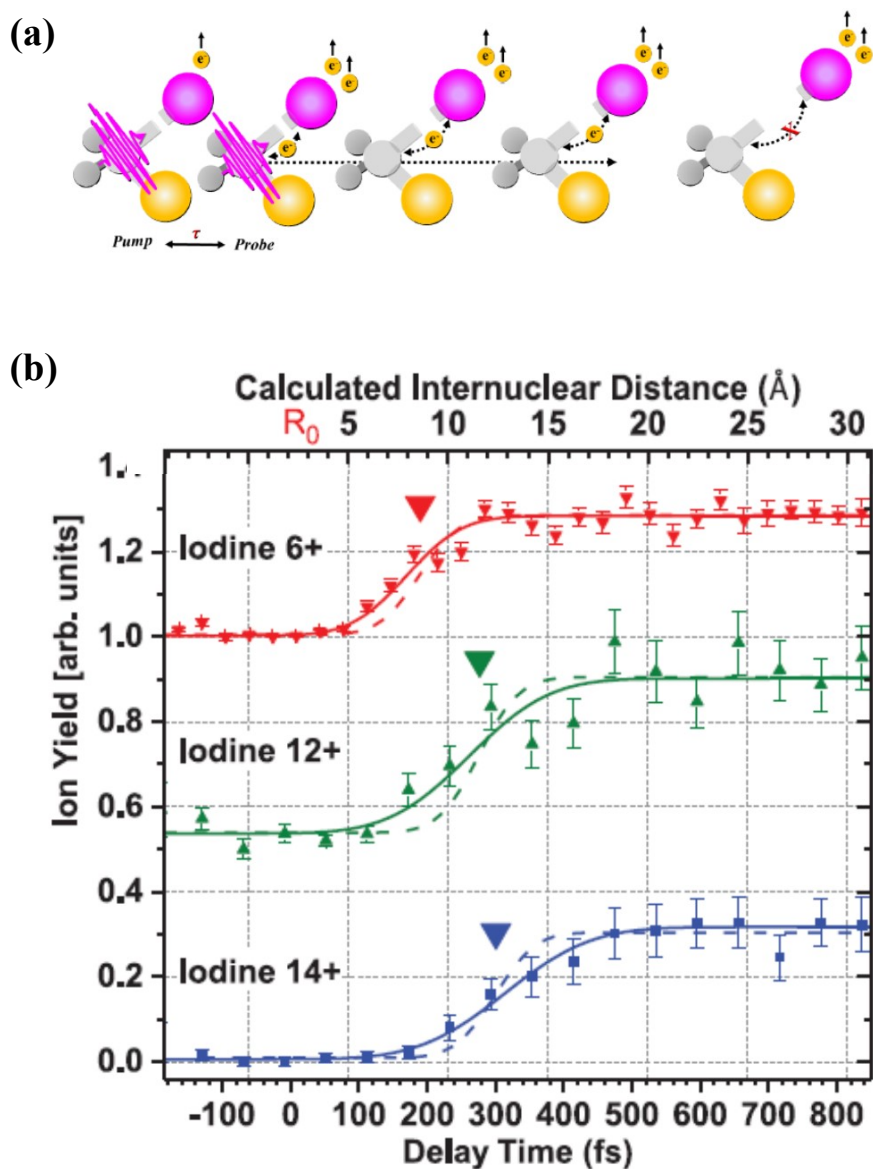


Figure 2.12: XUV pump-probe scheme for distance-dependent charge transfer in halomethanes. Here, XUV pump pulse creates dissociation channels containing neutral methyl and halogen ion fragments. Later on, at each delay (τ), XUV probe pulse kicks extra electron from the halogen ion and leads to asymmetric channel containing doubly charged halogen ion.

partner to remain neutral and, thus, reflect the distance-dependent ET probability, which is nearly 1 at small delays, and becomes negligible at large delays and internuclear separations.

In [87] [74] these observation were rationalized employing the classical over-the-barrier (COB) model which had been developed to describe charge transfer in ion-atom collisions [88] [89]. In the COB model, a purely one-dimensional function is used to describe the potential energy barrier,

$$V_e(r, R) = \frac{-p'}{R - r} - \frac{q}{r} \quad (2.3)$$

where R and r are the nuclear and electron coordinates. p' and q are the effective charges of the electron donor and acceptor, respectively. The electron is shared between the two groups as long as its binding energy is higher than the maxima of the potential barrier. The critical distance is determined by matching the binding energy in presence of the Coulomb field and the maxima of the potential barrier,

$$V_{max}(r, R) = E_i - \frac{q}{R = R_c}, \quad R_c = \frac{-p' + 2\sqrt{p'q}}{|E_i|} \quad (2.4)$$

where E_i is the binding energy of the outermost electron of the isolated donor. The electron is classically localized at one side while the internuclear distance is longer than the critical distance, where the ET becomes classically forbidden.

The predictions of the COB model, shown as triangles and dashed lines in Fig. 2.12 (b) could describe most of the basic experimental findings for inner-shell experiments [as well as in many other studies [87] [74], [76] [77] [79] [80] [90] [85], although the results of Ref. [74] suggested certain deviation from such classical behavior. Quantum mechanically, the ET probability in a simple donor-acceptor system in basic donor-acceptor systems depends on the interstate coupling (V_{AD}), which is determined by the overlap of the exponential tails of the two wave functions corresponding to donor (D) and acceptor (A) sites. It is expected to decrease exponentially with increasing internuclear distance (R_{AD}) as $V_{AD} = \exp[-R_{AD}/R_0]$, where R_0 is a characteristic parameter related to distance [74]. Correspondingly, the ET probability is expected to decreases exponentially with internuclear distance R_{AD} , thus,

significantly deviating from the COB expectations below the critical distance R_c . However, in most of the above-mentioned experiments, the temporal resolution was not sufficient enough to explore such deviations. One specific reason for this is an inherent jitter between the FEL and external optical laser [91] [77]. To overcome this, it was suggested to exploit XUV-pump – XUV probe schemes available at FEL facilities. However, so far these single-color pump-probe experiments focused on inner-shell ionization, which typically results in doubly charged states after photoionization and Auger decay and, thus, triggers very fast molecular separation via Coulomb explosion [87] [87].

Since the initial experiment [74] as well as some later studies (see e.g., [52]) relied on valence ionization and subsequent dissociation of the molecule in low-lying cationic states, a similar range of dissociative ionization pathways can be accessed by a single XUV photon. This opens a way towards XUV pump – XUV probe studies monitoring similar dynamics with significantly improved temporal resolution. The goal of the FEL part of this work is to exploit such possibility along with our capabilities to map dissociative ionization pathways, to address the issue of distance dependence of the ET probability in dissociating molecules upon valence-shell single-photon ionization. We use CH_3I and CH_2ICl molecules as test systems for these studies since ionization and, specifically, dissociative ionization of these systems by a single XUV photon is well-characterized via single-pulse experiments at synchrotrons (see e.g. [92] [93]). These pathways bear many similarities to the strong-field induced dissociative ionization exploited in [74] [52], and are slow enough to provide sufficient internuclear distance resolution in XUV-XUV pump-probe experiments.

2.5 Coulomb explosion simulation of light-induced molecular dynamics

One of the main components of the work presented in this thesis is the so-called Coulomb explosion imaging (CEI) technique used to study light-induced molecular dynamics. As briefly discussed in the Introduction, this approach relies on rapid few-electron ionization

and subsequent breakup of the molecule, driven by the strong Coulomb repulsion. If the ionization and fragmentation process takes place on a time scale that is much shorter than the time scale of nuclear motion, the corresponding breakup (“Coulomb explosion”) pattern carry information about the initial molecular geometry. Besides the necessity for instantaneous “vertical” ionization transition, this scheme implies that the charges are quickly localized at the corresponding nuclei upon ionization. As discussed at the end of section 2.3, this is often not a good assumption for double or even triple ionization of a bound molecule, where the dicationic or tricationic potential curves or surfaces deviate significantly from the purely Coulombic ones. This becomes a very reasonable approximation if the molecular bonds are broken, i.e., if the molecule dissociates, because at large internuclear separations the potentials quickly approach the Coulombic ones. It is also fulfilled much better for higher charge states, where the potential surfaces approach the Coulombic limit. However, for laser ionization, the time window for reaching these charge states might increase significantly. For example, if the required high peak intensity is $\sim 10^{15}\text{W}/\text{cm}^2$, even at 10 % of this intensity, single ionization can be already saturated and, thus, can happen early in the rising edge of the pulse. Since, as discussed in section 2.3, the dominant mechanism for reaching high charge states in strong-field irradiated molecules is sequential electron ejection at different times within the laser pulse, the time between the first and the last ionization step can, in fact, exceed the “nominal” pulse duration. Correspondingly, the molecular geometry can evolve on one of the intermediate ionic states during this window.

Despite all of the above limitations, CEI has proven to be a powerful tool for both, distinguishing between different “static” molecular configurations [94], and for mapping light-induced reactions [30] [27]. While a direct reconstruction of the geometry has not been achieved for polyatomic systems, the experimental CEI patterns provide a very detailed set of kinematical constraints on possible geometries or reaction scenarios, which can be compared to theoretical predictions via modelling. This is particularly efficient for the experiments performed in the coincidence mode, where the exact final charge state of each fragment is uniquely defined. A typical modelling scheme for CEI contain two steps: (1) the calculation of initial geometry (static or as a function of time) and (2) the simulation of the CE itself,

connecting the specific geometry with the experimental observables. The first step can just rely on a known geometry, or use any available level of theory to predict static or dynamic set of nuclei positions. Serious theoretical treatment of the second step, i.e., the calculation of multiple ionization and fragmentation by an intense laser field represents a severe and, in most of the cases, hardly solvable challenge. However, to discriminate between different geometries or reaction scenarios, a straightforward classical simulation based on the “instantaneous” Coulomb model is often sufficient. Below, a brief description of the implementation of such model in this work is presented, along with a few predictions for the exemplary photoreactions in halomethanes discussed in previous sections.

Coulomb explosion modelling

The simulation of the CE pattern starts with a given initial geometry. For a “static” simulation, this typically means the equilibrium geometry of a neutral molecule (although one can perform the simulation for any specific geometry of interest, either known or assumed – e.g., for different isomers, for a ground or excited state of the ion, etc.). The final state is assumed to be a set of localized point charges and point masses, where all the masses are located at exactly the same positions as the nuclei in the initial state, all of them initially at rest. For the simulation involving atomic fragments, the charge and mass points just coincide. For cases where one of the fragments contains two or more atoms, the charge is assumed to be localized at one point – typically at their center of mass. At the equilibrium distance, this can be a very coarse approximation for some break up channels, like, for example, molecular halogen formation. Even though one can achieve the values somewhat closer to the experiment modifying the charge distribution, in most of the cases discussed here we did not attempt this since such attempt would rely on a set of molecule-specific assumptions, which would be hard to generalize. Only the motion of the ions is considered for these simulations.

The motion of ions is described numerically assuming the motion of the individual ion (a point mass) is governed by the 2nd Newton’s law $\vec{F} = m\vec{a}$. If $\mathbf{r}(t)$ is the position vector of a ion having mass ‘ m ’ in three-dimensional space, then the differential equation governing

its dynamics is $r''(t) = F[r(t), r'(t), t]/m$. . . (1) where F is the total force acting on the ion, and r' and r'' are the first and second time derivatives of r . To study the motion numerically, we solved two coupled first-order equations: (1) $r'(t) = v(t)$, and (2) $v'(t) = F[r(t), v(t), t]/m$. These sets of equations are integrated over a time interval, usually 0 to 10 μ s, with a constant time step Δt . The 4th order Runge-Kutta algorithm is applied to solve the coupled differential equations for given initial input positions and velocities. The output positions and hence, velocities are used to calculate the final 3D momentum vectors of the ionic fragments. From those, any experimental observables, such as individual kinetic energies (KE) of the ions, their absolute or relative emission angles, or the total kinetic energy release (KER) of all fragments can be calculated.

Examples of static CE simulations for two-body and three-body breakup

Equilibrium geometry of three halomethane molecules used in this work is sketched in Fig. 2.13 and summarized in Table 2.2.

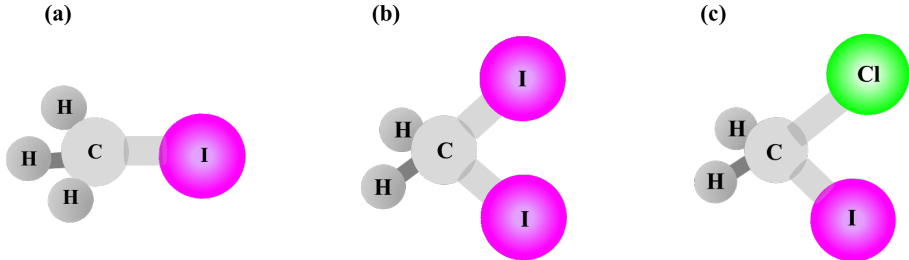


Figure 2.13: Sketch of molecular target: (a) CH_3I (b) CH_2I_2 , and (c) CH_2ICl

Geometry Molecule	C-H ($\text{\AA}$)	C-X ($\text{\AA}$)	$\angle$ H-C-H (deg.)	$\angle$ H-C-X (deg.)	$\angle$ I-C-X (deg.)
CH_3I	1.0721	2.2082	111.4	107.0	
CH_2I_2	1.081	2.170	111.7	107.3	116.4
CH_2ICl	1.081	2.181 (I) 2.161 (Cl)	112.1	106.6 (I) 108.6 (Cl)	114.4

Table 2.2: Equilibrium geometry of neutral ground state of halomethanes (CH_3I , CH_2I_2 , and CH_2ICl) where X represents I, Cl. Here, geometry values are taken from the references [95] and [96].

Since the channels involving hydrogen atom detachment or proton emission are not seriously discussed in this work, from the kinematic point of view, we treat CH_2 fragment (or CH_3 for the case of CH_3I in Chapter 6) as a point-like mass, such that CH_3I is effectively treated as a diatomic, and di-halomethanes as triatomic molecules. Correspondingly, the considered two-body CE final states for both di-halomethanes (CH_2I_2 and CH_2ICl) are $\text{CH}_2\text{X}^{n+} + \text{I}^{m+}$, $\text{CH}_2\text{I}^{n+} + \text{X}^{m+}$, and $\text{CH}_2^+ + \text{IX}^+$, where n and m can be 1 or 2, and $\text{X} = \text{I}, \text{Cl}$. For each of these two-body channels, the total KER is given by

$$\text{KER} = 14.4 \frac{mn}{R}, \text{ in [eV]} \quad (2.5)$$

where, $R [\text{\AA}]$ is the separation between the fragments. Knowing only the KE of one of the fragments, it is possible to determine the KE of the co-fragment from the conservation of linear momentum (neglecting the momenta of the much lighter electrons) from the following simple relations:

$$\text{KE}_B = \text{KER} \times \frac{M_A}{M_{AB}} \quad (2.6)$$

$$\text{KE}_A = \text{KER} \times \frac{M_B}{M_{AB}} \quad (2.7)$$

$$\text{KER} = \text{KE}_A + \text{KE}_B \quad (2.8)$$

where, KE_A and KE_B represents KEs of fragments A and B respectively with their corresponding masses M_A and M_B . M_{AB} is the mass of the molecule. Knowing the KE of one of the fragments thereby permits calculation of KE of the other co-fragment and the KER for that two-body channel. While all three quantities are directly measured in a coincident experiment, this relation is important for two-body breakup of molecular ions, where only one of the fragments is charged and, thus, detected in a typical experiment.

The outcome of such static two-body CE simulation yields just one independent energy value determined by the internuclear separation R . Both fragments are emitted back to back, and, within the so called axial recoil approximation, their emission direction (the line con-

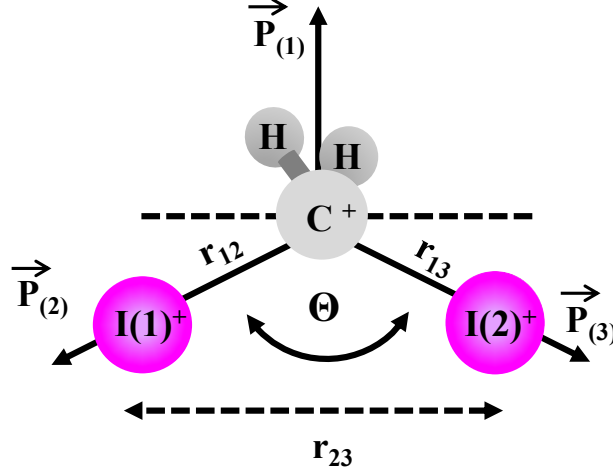


Figure 2.14: Cartoon showing the parameters used for the KER- Θ plot.

necting two center-of-mass points) is related to the spatial orientation of the molecular bond that is being broken. The representation of the observables becomes much more complex for a three-body breakup. As illustrated in Fig. 2.14 for the case of diiodomethane (CH_2I_2), the initial observables are three momentum vectors, whose vector sum is zero because of momentum conservation (again, neglecting the momenta of the electrons). The total KER, for our case given by the sum of the individual fragment's kinetic energy can be calculated as

$$\text{KER}[\text{eV}] = 14.4 \sum_{i,j} \frac{n_i m_j}{r_{ij}} \quad (2.9)$$

where $i = 1, 2, 3$ and $i \neq j$, is the separation of the two fragments in Å, whereas n_i and m_i are the charges of the corresponding fragments. Similarly, the angle between the momentum vectors of the two fragments (for example, the two iodines in Fig. 2.14) is given by

$$\Theta = \cos^{-1} \frac{[\vec{P}_{(2)} \cdot \vec{P}_{(3)}]}{|\vec{P}_{(2)}| |\vec{P}_{(3)}|} \quad (2.10)$$

where $\vec{P}_{(i)}$ is the momentum vectors of the i^{th} fragment. These two quantities can be directly plotted against each other, as shown in Fig. 2.15 (a). There, the simulated KER, Θ values for $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ three-body CE explosion are shown for two different initial

geometries: “regular” CH_2I_2 and “linearized” isomer $\text{CH}_2\text{I-I}$, as sketched in the figure.

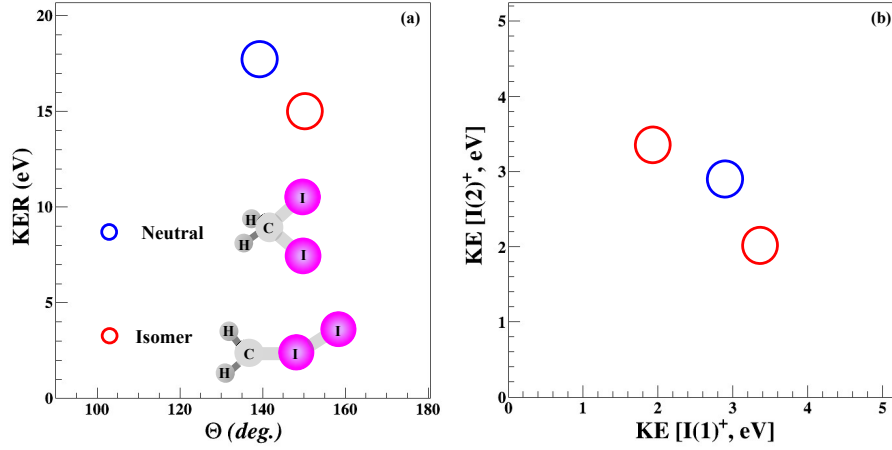


Figure 2.15: Three-body representation plots: (a) KER- Θ plot, and (b) KE sharing plot for iodine ions. In this plot, the blue circle represents the simulated values for “regular” CH_2I_2 and red circles are for “linearized” isomer $\text{CH}_2\text{I-I}$.

In Fig. 2.15 (b) the individual energies of the two iodine ions for the same breakup channel are shown against each other for these two geometry. From both panels, it is clear that the two configurations are expected to produce fragments which differ in KER, the emission angle between the two heavy fragments, as well as in their energy sharing. However, each of these graphs alone does not directly reflect the portion of energy carried by the 3rd fragment, or its emission direction. To address those points, there are two well-established complementary 2D representations of a three-body molecular breakup, known as Dalitz plots and Newton diagrams, respectively.

In the Dalitz plot [97], the three-body breakup events are represented in terms of fractional energies of the three fragments. In the Dalitz plot (see Fig. 2.16 (a)), the x and y coordinates are defined

$$\epsilon_x = \frac{\epsilon_{I(1)} - \epsilon_{I(2)}}{\sqrt{3}} \quad (2.11)$$

$$\epsilon_y = \epsilon_{\text{CH}_2} - \frac{1}{3} \quad (2.12)$$

where $\epsilon_i = e_i/\text{KER}$ and e_i is the energy carried by the i^{th} fragment after breakup. Thus, for the CH_2I_2 example the x-coordinate refers to the fractional energy difference between the

iodine fragments, whereas the y-coordinate represents the fractional energy carried by CH_2^+ . Correspondingly, this plot can be considered as an equilateral triangle of side length $\frac{2}{\sqrt{3}}$ with the inscribed ellipse. All events within the equilateral triangle obey energy conservation, while only the events within the inscribed ellipse obey the momentum conservation. For each point, the distance to each side of the triangle represents the fraction of energy carried by one of the fragments. The uncorrelated three-body events (which in the experiment could originate from false coincidences) are uniformly distributed throughout the plot. In Fig. 2.16 (a), the top point labeled as (1) represents the region where CH_2^+ carries all energy and I^+ fragments have zero energies (not allowed by the momentum conservation). The middle point labeled as (2) represents the region where CH_2^+ and each of the I^+ fragments are sharing equal energies, i.e. $\epsilon_{\text{CH}_2} = \epsilon_{\text{I}(1)} = \epsilon_{\text{I}(2)}$, whereas the point (3) at the bottom of the plot represents the configuration where CH_2^+ fragment carries no energy, which is then necessarily shared equally by the I^+ fragments: $\epsilon_{\text{CH}_2} = 0$; $\epsilon_{\text{I}(1)} = \epsilon_{\text{I}(2)}$. The symbols in the graph show the simulated points in the Dalitz plot for the main CH_2I_2 geometry and for the isomer sketched in Fig. 2.15.

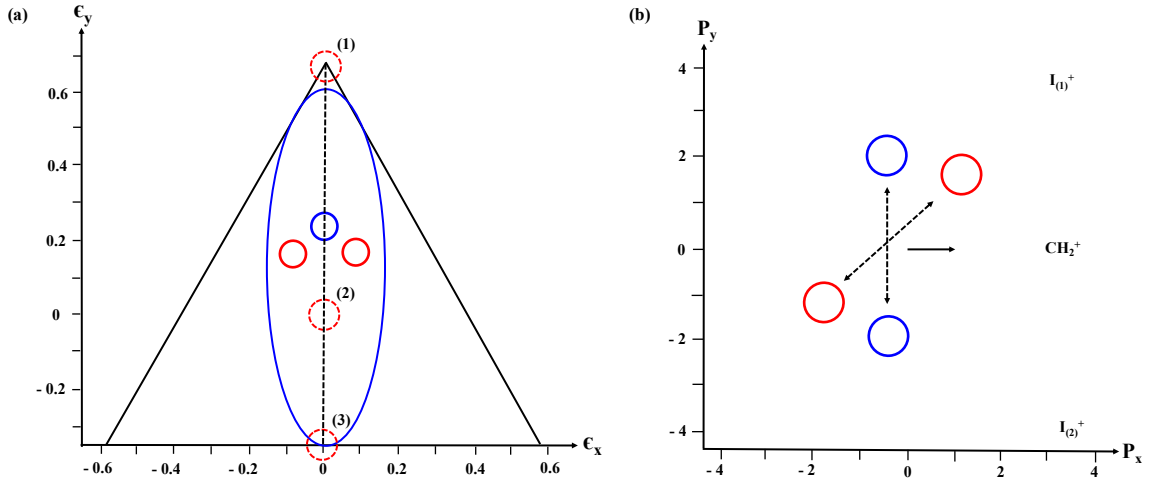


Figure 2.16: Three-body breakup representation plots: (a) Dalitz plot, and (b) Newton plot. In this plot, the blue circle represents the simulated values for “regular” CH_2I_2 and red circles are for “linearized” isomer $\text{CH}_2\text{I-I}$.

Complementary view of three-body breakup patterns focusing on angular correlations between the fragments is provided by the Newton diagrams. In such representation (illustrated in Fig. 2.16 (b) for the CH_2I_2 example), the momentum vector of the CH_2^+ is represented by

the vector pointing to the right, with its length fixed at one arbitrary unit. The magnitudes of momentum vectors of $\text{I}(1)^+$ and $\text{I}(2)^+$ fragments are normalized to the actual magnitude of the momentum vector of the CH_2^+ . Such normalized momentum vectors of the 1st and the 2nd iodine fragments are then shown in the lower and upper half-plane of the plot, respectively. As can be seen in the Fig. 2.16 (a), where the Newton plots simulated for the three-body CE of two different geometries of diiodomethane are shown, the vectors of the iodine ions reflect the possible geometry of the molecule with respect to the axis given by the CH_2^+ momentum.

Modelling dissociation channels in CEI pump-probe experiment

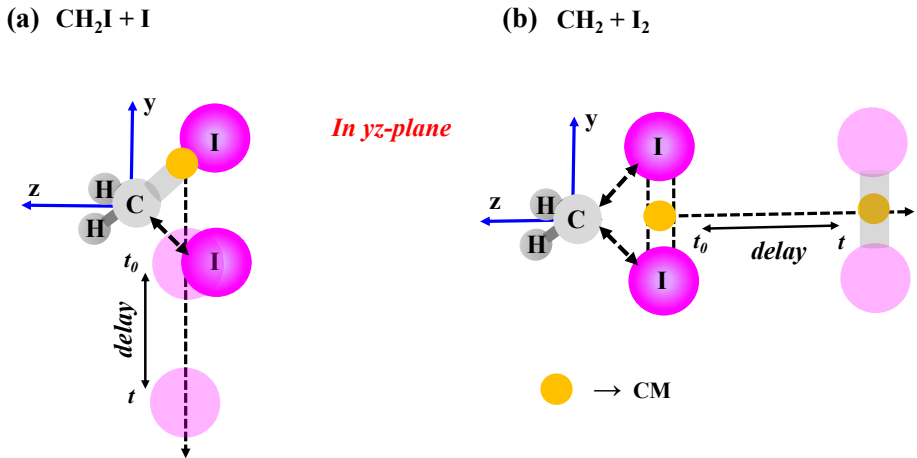


Figure 2.17: Cartoon showing scheme for numerical simulation of delay-dependent observables.

While the above discussion dealt with static version of CEI, the main goal of this work is to map time-dependent molecular geometry, i.e., to visualize how the positions of the nuclei evolve in time. To achieve this goal, the observables discussed above must be simulated for the geometry reached at different times, corresponding to particular pump-probe delay in the experiment. The CE simulation itself then models the probe step, whereas the geometry at each given delay is determined by the reaction triggered by the pump. To illustrate this approach, and to define some initial expectation for the experimental observables, we discuss here a very simplistic classical model for a couple of dissociation channels in diiodomethane.

As sketched in Fig. 2.17, we start from the (known) initial neutral equilibrium geometry of the molecule in the ground state. In the most trivial version of the simulation, we assume that for a given two-body dissociation channel triggered by the pump pulse, the two dissociating partners move as “fixed in space” rigid bodies along the axis connecting the centers of mass of both fragments. The velocity of this separation is set to the asymptotic dissociation velocity defined from the experimentally determined translational energy. This very simplistic approach yields a set of molecular geometries for each delay. In a second step, the same static CEI simulation as describe above (the probe step) is performed at each delay using the calculated geometry. For each delay, either two-body or three-body CE final state can be employed as a probe. The time-dependent KER for this step is then given by the equation 2.13, but with the addition of (translational) dissociation energy:

$$\text{KER}[\text{eV}] = 14.4 \frac{mn}{R(t)} + E_{diss}, \text{ in eV} \quad (2.13)$$

In the most naive model, the dissociation velocity is assumed to be constant, and reached its asymptotic value “instantaneously”, i.e., at the first non-zero delay point. In a somewhat more realistic scenario, the dissociation velocity starts at 0, and exponentially increases towards its asymptotic limit, with the rise time determined from the experimental data for that dissociation channel [86]. Correspondingly, E_{diss} in equation 2.13 also becomes time-dependent, until its asymptotic value is reached. In a more elaborate model, the molecular fragments like CH_2I are also allowed to rotate around their center-of-mass, while dissociating.

There are two ways to obtain the asymptotic translational energy for a given dissociation channel. If the pump pulse triggers a dissociative ionization channel, such that one of the dissociating fragments is charged, the energy of this ionic fragment can be measured in a single-pulse experiment using the pump pulse only. The energy of the neutral partner can be then recalculated using the relations (2.6-2.8). To ensure that in such non-coincident, single-ion measurement there is no contribution from the breakup of higher charge states, we compare the corresponding KE distribution with those obtained from all coincident channels involving this fragment, and excluded the corresponding contributions, typically at high

energies. However, this method to determine the “asymptotic” dissociation energy would not work for dissociation of a neutral molecule, where the fragments remain neutral and cannot be detected using our experimental approach. In these cases, the corresponding value of the asymptotic energy can be deduced from a CEI pump-probe measurement at very large delay, where the separation of the fragments is very large and, thus, the Coulomb repulsion becomes negligible.

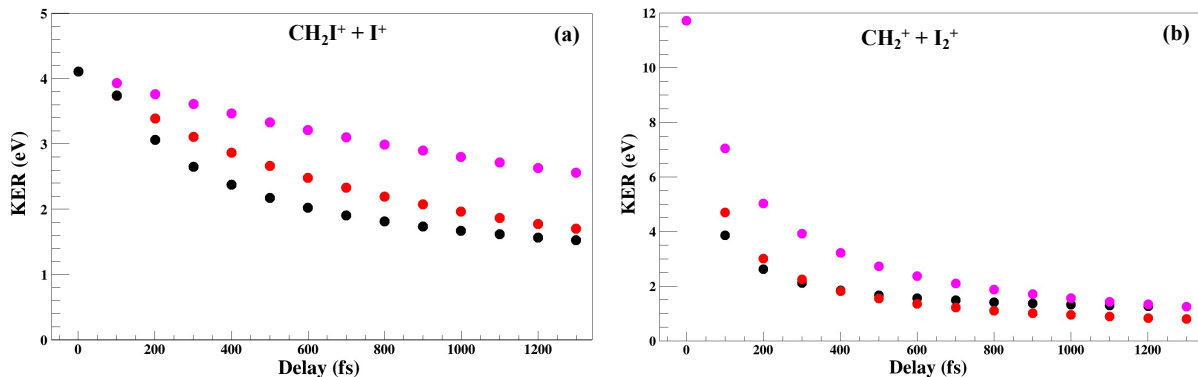


Figure 2.18: Delay-dependent KER under the scenario of instantaneous double ionization and hence, Coulomb explosion of dissociating channel created by pump pulse. Final state after probe pulse is: (a) $\text{CH}_2\text{I}^+ + \text{I}^+$, and (b) $\text{CH}_2^+ + \text{I}_2^+$. Colored circles represents the pathway, (a) involving CH_2I fragments, and (b) involving I_2 fragments, for different KER values at an interval of 100 fs. Here, “black” circles represent higher KER values and the “pink” circles represent smaller KER values used for the simulations.

Figure 2.18 displays two examples of the outcome of such simulation, showing the calculated KER as a function of pump-probe delay for the CH_2I_2 dissociation into CH_2I and I (a) and $\text{CH}_2 + \text{I}_2$ (b) fragments triggered by the pump pulse. The final state in the probe state (after the probe) is selected to be $\text{CH}_2\text{I}^+ + \text{I}^+$. The simulation is performed for three different dissociation energies. The descending lines in both cases reflect the increasing internuclear separation and, thus, weaker Coulomb repulsion. A very high KER at small delays in Fig. 2.18 (b) reflects the fact that for I_2 ejection the assumption of a point charge at I_2 center-of-mass is a very inadequate representation of a real charge distribution in the (still) bound molecule. Note that for these channels the curves cross each other: the one with the highest energy (black) moves faster towards large R and, thus, small KER, but becomes “flat” (approaching the region where $1/R$ is negligible) earlier than the others. However,

since the asymptotic energies for the other curves (e.g., for the red one) are smaller, the curves cross. The crossing with the black curve, as well as all the crossing in panel (a) occur at larger delays, outside the displayed delay range.

Here, it should be noted that the CE simulation (or the experiment) does not provide direct information about the charge state of the intermediate molecular configuration produced by the pump. In this specific example, the intermediate configuration in Fig. 2.18 (a) could be $\text{CH}_2\text{I} + \text{I}$, $\text{CH}_2\text{I}^+ + \text{I}$ or $\text{CH}_2\text{I} + \text{I}^+$ ($\text{CH}_2 + \text{I}_2$, $\text{CH}_2^+ + \text{I}_2$ or $\text{CH}_2 + \text{I}_2^+$ in Fig. 2.18 (b)). The obtained delay-dependent KER values are solely determined by the nuclear positions and the dissociation energy. However, in certain cases, different charge states (or electronic states of the neutral or of the ion) can be separated just by their dissociation energy and, thus, by the shape of the corresponding pump-probe curves in Fig. 2.18.

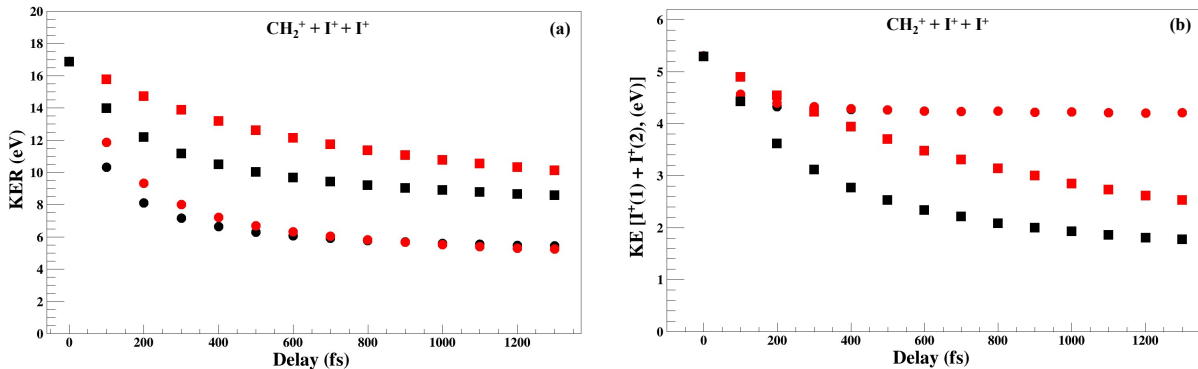


Figure 2.19: Delay-dependent three-body plots under the scenario of instantaneous triple ionization and hence, Coulomb explosion of dissociating channel created by pump pulse. Final state after probe pulse is $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$: Fig. (a) Delay-dependent KER distribution, and (b) Delay-dependent Sum KE of coincident iodine ions. In the Fig. (a) and (b), ‘square’ represents the dissociating channel involving CH_2I fragments and ‘circle’ represents the dissociating channel involving I_2 fragments. Here, ‘black’ circles represent higher KER value and the ‘red’ circles represent smaller KER value used for the simulations at an interval of 100 fs.

Figure 2.19 display the simulation for the same dissociation pathway as Fig. 2.18, but probed via three-body CE final state, $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$. In Fig. 2.19 (a), the simulated total KERs for both channels ($\text{CH}_2\text{I} + \text{I}$ and $\text{CH}_2 + \text{I}_2$) are plotted, whereas Fig. 2.19 (b) shows the sum KE of the two iodine ions, without considering CH_2^+ energy. Noticeably, while the I_2 elimination channels results in lower KER values in panel (a), it converges to larger sum

KE of the two iodines in panel (b). It reflects the fact that for this channel at large delays, the Coulomb repulsion with CH_2^+ plays a minor role, and the energy of the I^+ fragments is essentially determined by the CE of the bound I_2 molecule. For $\text{CH}_2\text{I} + \text{I}$ channel, instead, the detached iodine has low KE because of its large separation, and the KE of the second iodine one is determined by the CE of the bound CH_2I , where the CH_2 partner takes most of the energy because of momentum conservation.

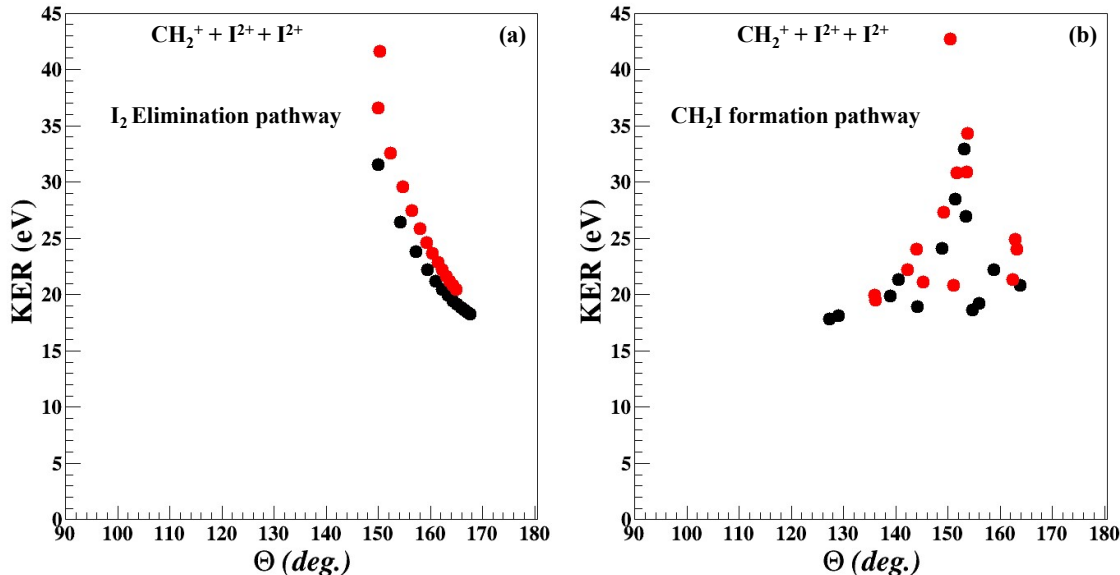


Figure 2.20: KER- Θ plot showing simulated values for dissociating pathways in the co-incident channel $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$: (a) I_2 elimination pathway, and (b) CH_2I formation pathway. Here, “black” circles represent higher KER values and the “red” circles represent smaller KER values used for the simulations.

For I_2 elimination channel at large delays one can also intuitively expect a nearly back to back emission of both iodine ions. To illustrate this, in Fig. 2.20 (a), we plot the simulated KER values for this channel as function of the angle between the iodine momentum vectors, integrated over the delay range plotted in Fig. 2.19, but probed via even higher final charge state, namely $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ channel. As we can see in the figure, this channel does converge towards 180° , as expected. In Fig. 2.20 (b) the simulation for $\text{CH}_2\text{I} + \text{I}$ channel probed via the same five-fold charged final state is presented for comparison. In this case, the molecular fragment (CH_2I) experiences rather high torque since the dissociation along the axis connecting two centers-of-mass is offset in angle with respect to the broken C-I

bond [98]. Therefore, to make a simulation more realistic, we allowed the CH₂I fragment to rotate with a period of 370 fs, taken from the recent simulation of the UED data [50]. The resulting distribution is rather broad in angle, sampling different orientations of the rotating co-fragment.

Chapter 3

Experimental Details

Time-resolved studies of light-induced dynamics in molecules employing coincident ion imaging as a probe, rely on two basic components: ultrafast femtosecond light source and ion momentum spectrometer. In the pump-probe experiments described here, three different types of laser pulses were used: 25 fs, 800 nm Ti:Sa pulses from the PULSAR laser at the James R. Macdonald Laboratory (JRML); their 3rd harmonic at 266 nm; and 30 fs, 53 nm XUV pulses from FLASH II FEL facility in Hamburg, Germany. Both experiments at the JRML and at FLASH employed the so-called “reaction microscope” or COLTRIMS (COLd-Target Recoil Ion Momentum Spectrometer) setup, which was rather similar for both cases, and differed mainly by the light focusing scheme and achievable background pressures. In the following, a brief description of these essential experimental components is given.

3.1 Femtosecond light sources used at the JRML

PULSAR: 10 kHz Ti:Sa laser system

The NIR-NIR and UV-NIR pump-probe experiments on halomethanes are carried out using the output of the Prairie Ultrafast Light Source for Attosecond Research (PULSAR). This is a customized version of the KMLabs Ti:Sapphire-based Red Dragon system. We used linearly p-polarized output of this system with the central wavelength around 790 nm, pulse

duration of ~ 25 fs and maximum pulse energy of 2 mJ at repetition rate of 10 kHz [99].

The oscillator of the PULSAR laser system is based on a Titanium-doped sapphire lasing medium which has a broad fluorescence bandwidth (670 - 1070 nm) and is pumped by a continuous 532 nm Nd:YAG laser system. The wide gain bandwidth supports a large number of cavity modes. The Kerr-lens mode-locking technique is used to generate ultrafast pulses from the Ti:Sapphire oscillator with a repetition rate of 75.2 MHz. The oscillator output has central wavelength of 790 nm and bandwidth of about 80 nm with ~ 4 nJ pulse energy. The pulse duration is reduced to ~ 10 fs with the help of dispersion-compensating prisms in the oscillator.

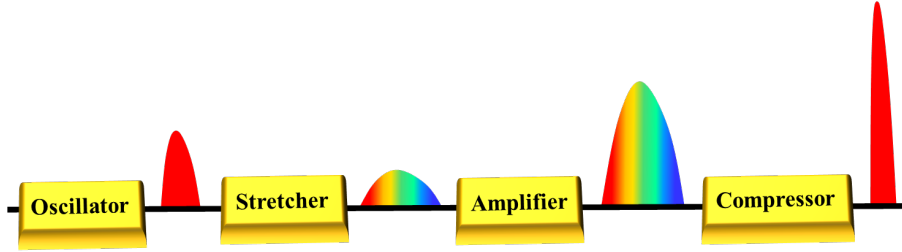


Figure 3.1: Working principle of the Chirp pulse amplification (CPA): An output of the oscillator is stretched in time which results in low-intensity pulse suitable for amplification purpose. This stretched pulse is fed into the amplifier and the amplified pulse is compressed in time. So, the final output is ultrashort and highly intense.

A typical mode-locked output from the oscillator is used to seed the amplifier. The amplification in the PULSAR laser system is based on the chirped-pulse amplification (CPA) technique [100]. This technique preserves the broad bandwidth and prevents damaging the amplifier and, in meantime, increases the pulse energy from nJ to a few mJ. In the CPA technique, the laser pulses provided by the oscillator are stretched in time from the femtosecond to the picosecond time scale with the help of stretchers based on a pair of diffraction gratings. The stretched pulses are selected by the Pockels cell, where the repetition rate is reduced to 10 kHz. Laser pulses undergo amplification in 2 stages. The first stage consists of 14 passes after which the pulse energy is almost 1 mJ. The second amplification stage further increases the pulse energy to about 2mJ in 5 passes. At the end, reverse stretching process is performed using grating-based compressor, yielding ~ 2 mJ maximum pulse energy (average power ~ 20 W). while the pulses directly after the compressor have $\sim$

21-23 fs duration, the typical pulse length in the interaction region was 25-27 fs.

3ω generation

High harmonic generation from the fundamental frequency (ω) is based on the non-linear behavior of the medium. The response of the medium to an applied optical field depends on the strength of the field. When an intense light is transmitted through a non-linear medium, an optical field polarizes the medium. The medium modifies the original field as the field propagates through it and changes its phase and also adds new frequency components.

If $\mathbf{P}$ is the polarization and $\mathbf{E}$ is the electric field, then polarization and electric field are related as:

$$\mathbf{P} = \chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{E}^2 + \chi^{(3)}\mathbf{E}^3 + \dots \quad (3.1)$$

where, $\chi^{(1)}$ is the linear susceptibility. This linear relationship holds at the low intensities. At high intensities, which are usually provided by the ultrashort lasers, the linear relationship between $\mathbf{P}$ and $\mathbf{E}$ is no longer valid. In this case, higher terms of susceptibilities, $\chi^{(2)}$ and $\chi^{(3)}$ which are the second- and third-order nonlinear susceptibilities respectively, become dominant. The medium is said to be nonlinear when the higher-order terms are not negligible compared to the linear term.

To generate laser pulses with 3ω frequency, there is second harmonic (2ω) generation (SHG) process accompanied by the sum frequency generation (SFG) process [101]. If the electric field ($\mathbf{E}$) is written as $\mathbf{E} = \mathbf{E}_0 e^{-i\omega t}$, then the second order polarisation ($\mathbf{P}^{(2)}$) term can be expressed as:

$$\mathbf{P}^{(2)} = \chi^{(2)}\mathbf{E}_0^2 e^{-i(2\omega)t} \quad (3.2)$$

The term 2ω , twice of the fundamental frequency, in above expression 3.2 is called second harmonic and the process is called second-harmonic generation (SHG). The second-harmonic is generated through a phase matching process. For a SHG process, the phase matching condition is written as,

$$n_3\omega_3 = n_1\omega_1 + n_2\omega_2 \quad (3.3)$$

where, $\omega_1 = \omega_2 = \omega$ and $\omega_3 = 2\omega$. To fulfil this condition, we use birefringent crystals such as beta-barium borate (β -BBO). For the SHG process, the ω_3 can be an extraordinary wave and ω_1 is an ordinary wave so that phase matching condition is $n_e(2\omega) = n_o(\omega)$. A type-I β -BBO crystal with a cut angle of 29.2° and a thickness of $150 \mu\text{m}$ is used to generate second-harmonic laser pulses. For this crystal, the polarization direction of the fundamental wave (800 nm , ω) and the second harmonic (2ω) signals are perpendicular to each other.

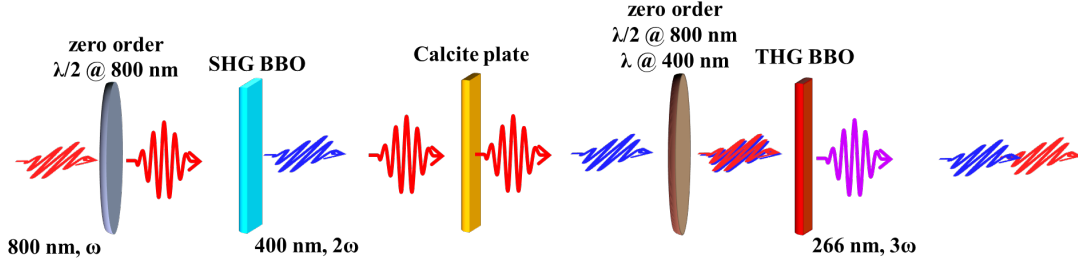


Figure 3.2: 3ω generation: p-polarised input ω signal is rotated such that input to the SHG BBO crystal is s-polarised ω signal. The output is p-polarised 2ω signal together with s-polarised ω signal. 2ω and ω signals have time delay between which is corrected after passing through calcite plate. Before passing through the THG BBO crystal, the ω signal is rotated so that both 2ω and ω signals are p-polarised with the help of dual half waveplate. Finally, output from THG crystal is s-polarised 3ω signal together with the p-polarised 2ω and ω signals which are separated later on.

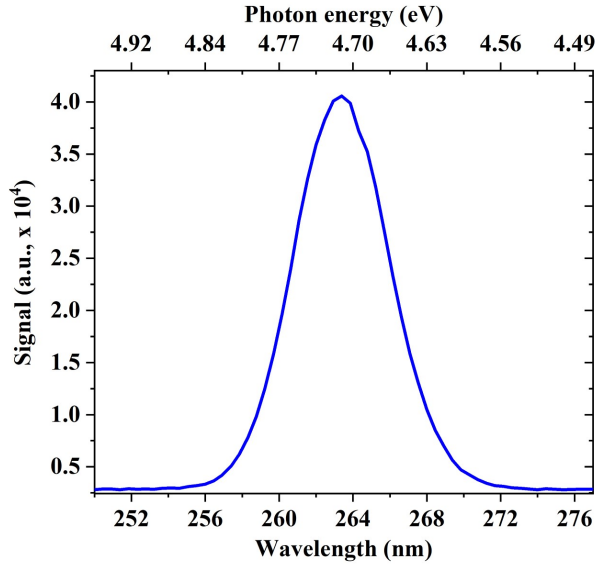


Figure 3.3: The measured UV Spectrum of the third-harmonic pulse.

Not only the polarisation are in different directions, there is also time delay between

the fundamental wavelength (ω) and second harmonic (2ω) signal. To compensate the time delay, a calcite plate is used and is tilted by a few degrees for fine tuning. After the calcite plate, the second harmonic pulses are ahead of the fundamental laser pulses in time. This is essential for the 266 nm, 3ω generation. To generate the 3ω efficiently, the polarization of the fundamental and second-harmonic have to be horizontal. A zero-order dual half waveplate ($\frac{\lambda}{2}$ for 800 nm and λ for 400 nm) is used to rotate the polarization of ω by $\frac{\pi}{2}$ from s- to p-polarized light. The passage through the waveplate causes the two pulses to nearly overlap in time. To generate 3ω through the SFG process, the ω and 2ω signals are allowed to overlap temporally and spatially in a type-I β -BBO crystal with a thickness of 20 μm and cut angle of 44.3° . The 3ω pulse is then separated from 2ω and ω signals using reflective beamsplitters. The output 3ω pulse are compressed in a prism-pair compressor to ~ 45 fs (FWHM in intensity) before sending into experimental chamber. The pulse duration of the UV pulses is determined using the cross-correlation measurement of Ar^+ signal and the difference frequency generation (DFG).

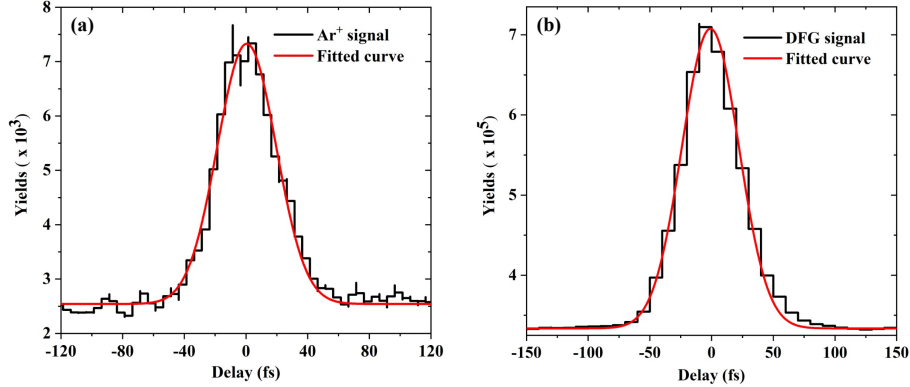


Figure 3.4: UV-IR cross correlations: (a) Ar^+ signal in COLTRIMS and (b) Difference frequency generation (DFG)

The pulse duration of the UV pulses on the laser table, before entering the COLTRIMS chamber, is determined using the difference frequency generation (DFG) [101]. The pulse duration in the chamber itself is verified by measuring the cross-correlation of the 800 nm and 266 nm pulses provided by the delay-dependent Ar^+ ion yield. Fig. 3.3 shows a typical UV spectrum, while the cross-correlation spectra measured using Ar^+ signal in COLTRIMS

and using DFG, are shown in Fig. 3.4 (a) and (b), respectively.

3.2 Ion imaging system

When a molecule is exposed to an intense femtosecond laser field, the laser-molecule interaction can be very complicated. This interaction can result in many possible reaction channels ranging from neutral excitation and single ionization to dissociative ionization and Coulomb explosion (CE) channels. A powerful way to characterize these channels is to measure the 3D momenta of the fragments belonging to that particular reaction channel. In order to achieve this, we need experimental setup which provides high momentum resolution, full solid angle (4π) particle collection, and enables coincidence measurements. One of the experimental setups which fulfill these criteria is the so-called “reaction microscope” (REMI) [102] [103]. These machines normally focus on the detection of charged particles and combine momentum imaging capabilities for ions and electrons. The expression “reaction microscope” is often interchanged with the term COLTRIMS, which stands for COLd Target Recoil Ion Momentum Spectroscopy and, in its original meaning, does not include electron detection [104]. A “reaction microscope” is therefore essentially a COLTRIMS (or RIMS if the target used is not actually cold) combined with a large open-area electron spectrometer. Neutral reaction products are not detected in such setup, although they can be measured in coincidence with ions in ion beam experiments [105].

Both experimental setups used in this work, at the JRML and at FLASH-II facility are actually “reaction microscopes” capable of detecting both, ions and electrons. However, in all of the experiments described in this thesis, only the ion part was used, such that they represent typical COLTRIMS measurements.

The spectrometer used at the JRML is based on the design developed in [106]. The experimental setup used for NIR-NIR pump probe experiments is identical to that described in [24] and combines the ion imaging spectrometer with a Mach-Zehnder type interferometer for varying the delay between the two NIR pulses. The essential components of the COLTRIMS setup itself are supersonic gas jet, ultrahigh vacuum (UHV) chamber, a spec-

trometer providing homogeneous electric field and a time- and position-sensitive detector system.

Reaction Microscope (REMI)

Reaction Microscope (REMI) is a powerful tool for the study of molecular dynamics in intense femtosecond laser fields. This setup allows the measurements of the full 3D momentum vector of the charged fragments after irradiation of intense pulses with high resolution and 4π solid angle acceptance. This technique relies on the well localised interaction region and detection of the final charge state after the interaction. The time-resolved measurement of charged fragments is carried out using the pump-probe technique. We add Mach-Zehnder type interferometer equipped with the delay stage in the experimental beam path.

Details regarding REMI used for the pump-probe experiments mentioned in this thesis are explained in literature (see, e.g. [106] [87]). Here, I will briefly discuss the REMI setup. Essential components of REMI are supersonic jet, ultrahigh vacuum system (UHV), spectrometer, homogeneous electric field and detector system.

In order to study laser-induced molecular dynamics in a coincidence mode, the interaction region should be well confined so that we can carry out gas-phase experiment with, on average, less than one fragmentation event per laser shot. In order to resolve ion momenta, the translational temperature of a laser target needs to be well below the room temperature. This demands a well-collimated and internally cold molecular target. This kind of molecular target is prepared via the supersonic gas expansion followed by the collimation of the molecular jet. For this, gas is allowed to flow from a high pressure region, through a small nozzle (nozzle diameter is $30\text{ }\mu\text{m}$), into a low pressure region. As the pressure at the nozzle exit is higher than the ambient pressure, the gas is said to be “under-expanded”. As a result, the gas expands even further and pressure lowers. The pressure drop produces a supersonic expansion of the gas which cools the ensemble of molecules via collisions. The gas jet is guided through differentially pumped stages before it reaches the main chamber. The first stage behind the nozzle has the base pressure of $\sim 10^{-6}$ Torr (up to 10^{-6} Torr with

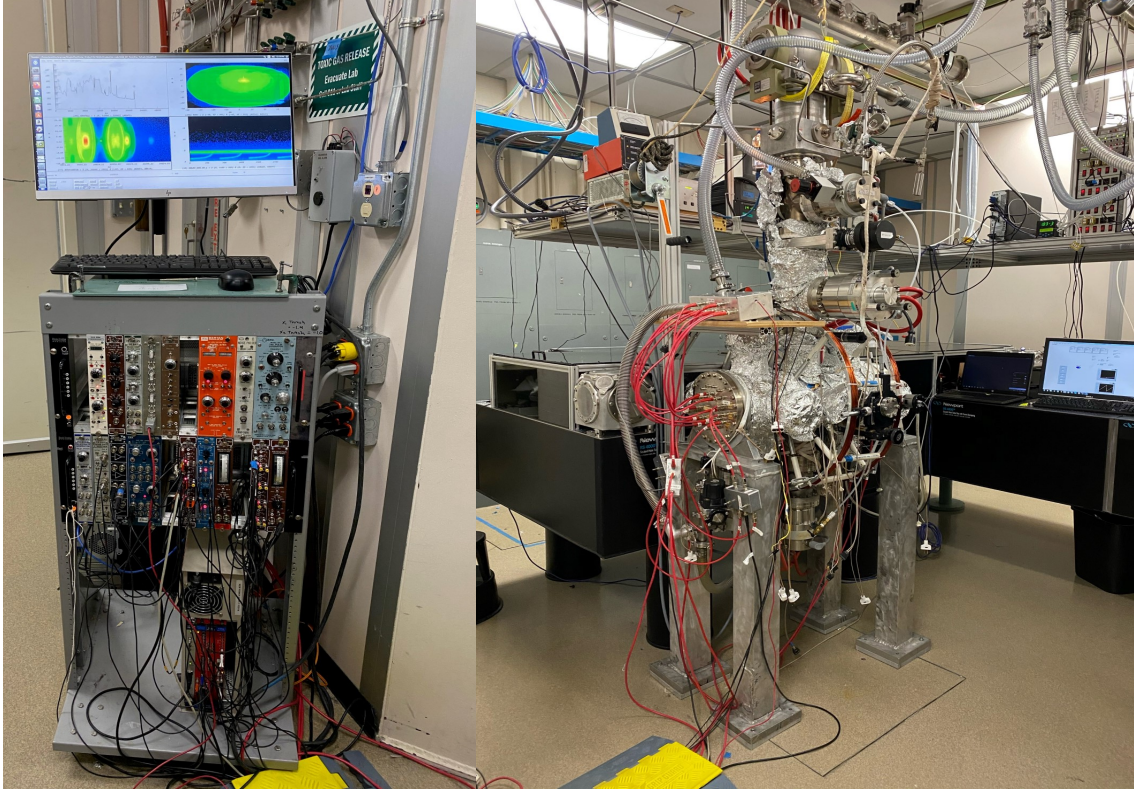


Figure 3.5: Experimental area of reaction microscope (REMI) setup for the time-resolved pump-probe experiment in JRML (PULSAR).

the gas jet on), which is highest in the entire vacuum system. Behind the nozzle, a so called “skimmer” with the opening of $200\ \mu\text{m}$ is placed co-axial to the nozzle which cuts the part of the expansion cone of gas. Then, the jet enters the second stage where the base pressure is $\sim 10^{-6}$ Torr and then, enters the third differential pumping stage from the second one by 1 mm opening. As a result of passing through skimmers and adjustable aperture, the gas jet is highly collimated when entering the main chamber. This minimizes the dissipation of gas from the jet in the main chamber and further reduces the base pressure in the main chamber, which is kept below 10^{-6} Torr in the absence of a gas target. There is a gate valve in-between the second and the third stage, which helps to isolate and maintain the vacuum in the main chamber for troubleshooting purposes. The opening between the third stage and the main chamber is 2 mm. Third stage also houses the mechanical slit for further collimating the jet in perpendicular direction. After passing the interaction chamber, the residual gas is collected in the “catcher”. The opening of main chamber to catcher is 6 mm. The UHV in

different sections of the reaction microscope is maintained with the turbo-molecular pumps backed by the roughing pumps.

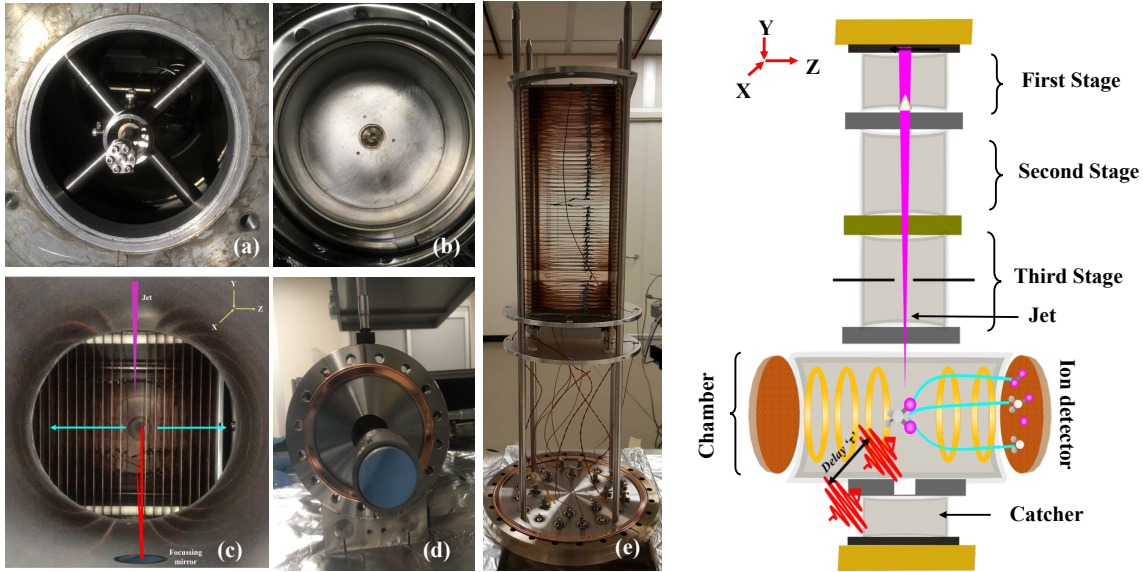


Figure 3.6: A sketch of the reaction microscope (REMI) setup for the time-resolved pump-probe experiment in JRML (PULSAR). On the left-hand side, images are numbered (a) to (e): (a) Nozzle and its holder, (b) Skimmer, (c) Interaction region, (d) Focussing mirror and its holder, and (e) Spectrometer. On the right-hand side, there is a scheme of REMI showing five sections including three different stages, chamber and catcher. The delayed and undelayed laser pulses going along X-direction after being focussed intersect with the supersonic molecular beam going downward along Y-direction. The resulting molecular ionic fragments are directed along the spectrometer axis (Z-direction) in presence of the homogenous electrostatic field.

In order to have a small interaction region and achieve high laser intensities, we need to have a focused laser beam on the thin molecular jet. For this, we used a spherical mirror ($f = 7.5$ cm) to focus the input laser beam at the jet inside the vacuum chamber. The position of the focusing mirror can be adjusted along the x, y and z direction by the 3D manipulator until the back-reflected beam is focused on the target jet.

After irradiation with the focused laser beam ionic fragments created in the interaction region needs to be directed towards the detector system. For this, there is series of copper plates of the same size and with holes at the center inside the vacuum chamber which constitute the “spectrometer” itself. The axis of spectrometer is parallel to the line connecting the interaction volume and the center of the detector and, thus, perpendicular to both, gas

jet and laser propagation directions. A homogeneous electric field is created within the spectrometer by uniformly decreasing the potential from left to right. With this homogenous field, the charged fragments can be guided towards the detector system.

The time- and position-sensitive detector system consists of microchannel plate (MCP) and the delay-line anodes (DLAs). This ensures 3D measurement of momentum vectors of a charged fragment produced in the molecular breakup. MCP is a fabricated plate which consists of an array of glass microchannels. The inside of each channel is coated with high-resistance semiconductor which serves as secondary electron multiplier. When two or more MCPs are operated in series, from a single input, a pulse of 10^8 or more electrons are generated. This avalanche of electrons results the charge emitted from the back surface of the MCP such that it can be measured electronically. The front part of the MCP detector on the ion side is biased with high (~ 2.4 kV) negative potential and the back is at ground. The voltage drop across the MCP gives the time of flight (TOF) information of the charged ion. The TOF of a charged particle is determined from the impact time on the detector with respect to an photodiode trigger signal as,

$$TOF = (t_{mcp} - t_{trigger}) \quad (3.4)$$

where, t_{mcp} is impact time on the MCP.

Apart from the TOF information of the fragments, we also need the 2D position information. For this, we use delay-line anodes (DLAs), which can be used to extract the position information of the fragment. This consists of a pair of bare copper wires isolated from one another and are wound across opposite edges of an insulating plate. One of the wires (signal) is maintained more positive (+ 50 V) than the other wire (reference). Doing so, electronic noise is induced in both wires while the electron signal is induced only in the signal wires. Later, the signals in the reference wire are subtracted from those on the signal wire and thus, eliminate the electronic noise induced in the wires. A signal from the impact position on the delay line propagates in perpendicular directions towards both ends. The difference of times taken to reach the ends in both directions give the position information of the signal. If t_1

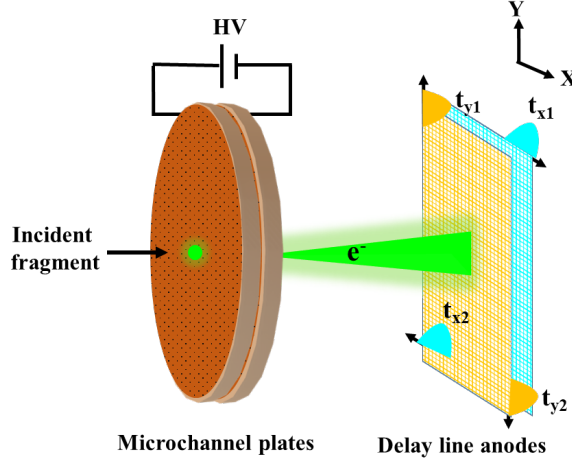


Figure 3.7: Working scheme of microchannel plate (MCP) and delay-line anodes (DLAs): MCP is a fabricated plate which consists of an array of glass microchannels. A single input ion in one of channel of MCP gives electron cloud, several thousand of electrons, as output from the rear side of the plate. Each MCP is connected to the power supplies via a load resistor. This electron cloud cause voltage drop over the resistor which is used to measure the TOF of charged fragment. DLAs is an arrangement of a pair of bare copper wires isolated from one another and are wound across opposite edges of an insulating plate. The electron cloud when lands on the DLAs gets accelerated towards two opposite ends in perpendicular directions. The arrival time difference in both directions give the position information of charged fragment.

and t_2 are the arrival times at the two ends of the line measured with respect to t_{mcp} , the impact position x is deduced:

$$x \sim (t_{x1} - t_{mcp}) - (t_{x2} - t_{mcp}) = (t_{x1} - t_{x2}) \quad (3.5)$$

$$y \sim (t_{y1} - t_{mcp}) - (t_{y2} - t_{mcp}) = (t_{y1} - t_{y2}) \quad (3.6)$$

The conversion factor for the timing (ns) signal into the position (mm), expressed in units of mm/ns, is extracted from the detector size. The position and timing signals are recorded by a multihit time-to-digital converter and stored in event-by-event mode file for off-line analysis. Like the time of flight information, the position information needs correction as the laser focus may not coincide with the centre of the detector which is done by subtracting an offset.

For physical interpretation of the data, time and position information of charged fragment

needs conversion into momentum information along x,y and z direction. In the experiment, z is the direction along the spectrometer axis which is perpendicular to detector plane (x,y).

$$p_z = \frac{m_i l}{t_i} - \frac{E q t_i}{2} \quad (3.7)$$

$$p_x = \frac{m_i x}{t_i} \quad (3.8)$$

$$p_y = \frac{m_i y}{t_i} \quad (3.9)$$

where, p_z , p_x and p_y are momentum along z, x, and y direction. Similarly, l is the distance of the detector from the interaction region and E is the value of the electric field over the length of the spectrometer.

3.3 Experiments at FLASH-2 FEL facility

The XUV-XUV pump-probe experiments on halomethanes have been carried out using free electron laser (FEL) source available at Deutsches Elektronen-Synchrotron (DESY), Hamburg.

Free Electron Lasers

Free- electron lasers (FELs) are based on the creation of radiation with laser-like properties from the accelerated electrons. In a typical FEL, first an electrode is irradiated with a pulsed laser to create photoelectrons. These emitted photoelectrons achieve relativistic energies in a linear accelerator. Then, the electron bunches enter an undulator which is a periodic arrangement of dipole magnets with alternating polarity. In the undulator, electrons move in the generated electromagnetic wave, arrange in its electric field and undergo the process of microbunching. Depending on the position in the field, electrons loose or gain longitudinal velocity and thus, electron bunch split up in microbunches. The distance between the microbunches is on the order of the FEL wavelength λ . One microbunch consist of N electrons oscillating like a single particle of charge $-Ne$. This leads to correlated emission

of radiation, which is fully coherent within one microbunch. Microbunching process enables the scaling of radiation power of FELs quadratically with the number of electrons in each microbunch. This makes FELs unique compared to other sources of undulator radiation such as synchrotrons.

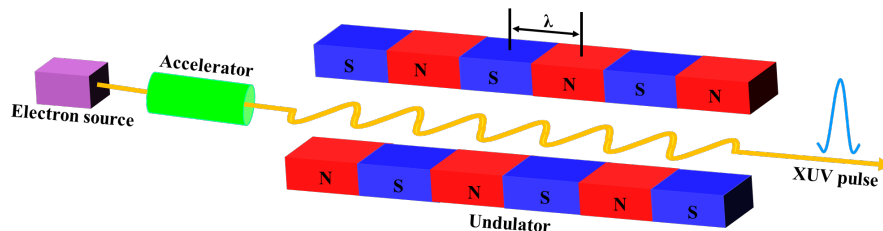


Figure 3.8: Scheme of Free electron laser sources (FELs): FELs consists of three main components: electron source, accelerator and undulator. An electron bunch enters the accelerator region where electrons are accelerated to relativistic speed. The electron bunch then undergoes deflections and the microbunching process in the undulator region. For the experiments described here, output is the XUV radiation of a certain spectral range.

Free-electron laser source (FELs) in DESY consists of one linear accelerator and two separate planar undulators which ends up in FLASH-1 and FLASH-2 facilities. Unlike FLASH-1, the undulator of the FLASH-2 branch can be moved which allows quick tuning of the wavelength independent of FLASH-1. The accelerator supplies electron bunches at a repetition rate of 10 Hz. The undulator modules are arranged in a way that they create a magnetic field perpendicular to the ground. So, the electrons' motion as well as the polarization of the FEL radiation is parallel to the ground. The output radiation of FLASH fills the wavelength range between 4 and 90 nm, with pulse energy of 1 - 500 μJ and pulse durations of 10 - 200 fs [107] [108].

Experiments with FLASH-2 ReMi

In our XUV pump-probe experiment, we used photon pulses having central wavelength of 53.2 nm, effective rep. rate of 400 Hz, pulse duration of ~ 30 fs and the pulse energy up to 5 - 10 μJ . We used a dedicated “reaction microscope” setup permanently installed at FLASH-II and operated by the crew from Max Planck Institute for Nuclear Physics, Heidelberg. The setup is described in details in [110]. However, in our experiment we used an older, back-

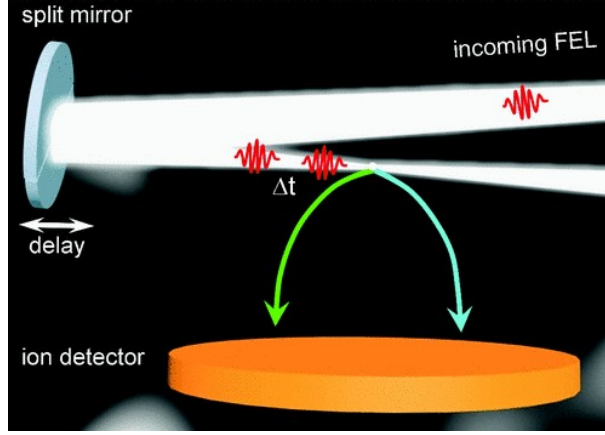


Figure 3.9: Schematic of the split-mirror setup for XUV-pump XUV-probe experiments combined with an ion momentum spectrometer (from [109]).

reflecting split-mirror setup for producing pair of pump and probe XUV pulses, as described in [109]. The setup is schematically depicted in Fig. 3.9. The pairs of XUV pulses were focused onto a dilute molecular jet in the middle of an UHV spectrometer chamber (base pressure $< 10^{-11}$ Torr). The ion extraction and detection procedure is very similar to the one described in section 3.2. The main difference is that the spectrometer and, thus ion time-of-flight axis is vertical for the FLASH-2 setup, while the XUV light polarization is horizontal.

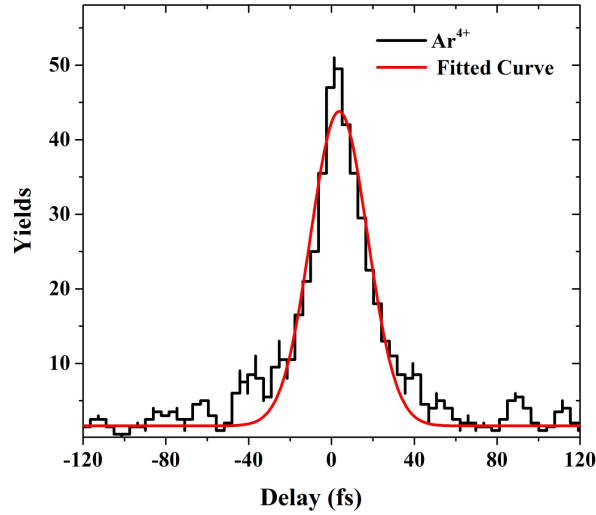


Figure 3.10: Autocorrelation trace of the FLASH XUV pulse measured using Ar^{4+} ion signal.

The temporal profile of the XUV pulses on target was characterized using autocorrela-

tion traces obtained from the non-linear ionization signal measured as a function of delay between the two pulse replicas [109]. An example of such an autocorrelation trace based on the measured delay-dependent yield of Ar^{4+} ions is shown in Fig. 3.10. Analysis of the experimental autocorrelation traces performed following the procedure described in [111] [112] confirms that the average duration of the XUV pulses is of order of 30 fs (FWHM).

Chapter 4

Strong-field induced dynamics in diiodomethane and chloriodomethane molecules in the near-infrared domain

As discussed in Section 2.3, a polyatomic molecular system exposed to an intense NIR field responds in a number of different ways. It can be excited (electronically, vibrationally and rotationally), singly- or multiply-ionized, dissociated and Coulomb exploded. In this chapter, experimental analysis of these dynamics is presented for two dihalomethane molecules, CH_2I_2 and CH_2ICl . We mainly focus on diiodomethane (CH_2I_2), and use the chloriodomethane results for comparison, in particular, for cases where the distinguishability of the two halogen atoms plays a role. We start with the discussion of the CH_2I_2 response to a single NIR pulse, and follow with the description of the pump-probe experiments employing pairs of NIR pulses to trigger and to probe the dynamics.

As discussed in Chapter 3, our experimental setup for these experiments is based on the reaction microscope (REMI) apparatus, and focuses on the detection of ions. In all of the JRML experiments described below we used linearly polarized output of the PULSAR laser

(see Section 3.1), a Ti:Sapphire-based system with a central wavelength of 790 nm and pulse duration of 25 fs, operating at a repetition rate of 10 kHz. This pulse duration is well-suited for this study since it matches the timescale of the vibrational modes of the molecules used as targets, as detailed in Table 4.1. The molecular jet temperature is estimated to be ~ 45 K (see Appendix B), such that nearly all the target molecules are initially in the ground vibrational state.

Modes			
Molecule	I-C-I bending	C-I sym. stretching	C-I asym. stretching
CH ₂ I ₂	^a 122 (123)	507 (493)	611 (584)
	^b 273.4 (271.2)	65.8 (67.6)	54.6 (57.1)
CH ₂ I ₂ ⁺	X A B C		
	^a 113 118 123 125	(540)	(500)
	^b 295.2 282.7 271.2 266.8	(61.7)	(66.7)

Table 4.1: Ground state frequencies for neutral and ionic geometry of CH₂I₂ molecule for different vibrational modes. Here, X corresponds to the ionic ground state while the A, B and C are the higher excited ionic states. Row (a) gives frequencies in cm⁻¹, and row (b) is the corresponding period in fs. Values in parenthesis represent the experimental values reported in [69] and [45].

The peak intensity of the laser pulse on target is determined using the Ne⁺ ion momentum distribution measured at low extraction field (A), which displays a characteristic kink at the recoil momentum value corresponding to emission of photoelectrons with 2Up kinetic energy [113]. The intensity values obtained using this approach agree with the values calculated from the measured beam parameters on a level better than 20%. The event rate was kept on a level below one event per laser shot, in order to enable coincident measurements of ionic fragments.

For time-resolved measurements, we tried different combinations of pump and probe intensities. For the measurements discussed here, we kept the intensity of the pump pulse around $\sim 2 \times 10^{14}$ W/cm² whereas the probe pulse is set to either to the same intensity as the pump, or to a larger value of $\sim 4 \times 10^{14}$ W/cm². The total count rate in the region where the pump and probe pulses do not overlap is kept ~ 6 kHz, which is well below the

repetition rate of the laser. This count rate ensures that, on average, we have less than one fragmentation event per laser shot, which is crucial for several reasons.

4.1 CH₂I₂ molecule under a single NIR pulse

Single-pulse measurements provide initial information on NIR-induced ionization and fragmentation pathways. It is thus crucial for interpreting the outcome of pump-probe experiments as it helps to understand what the pump and the probe pulses alone do to a molecule. Among other things, single-pulse data yield an overview of molecular dynamics triggered by the pump pulse, and also provide a reference for the delay-independent pathways in pump-probe measurements. This section discusses possible fragmentation pathways, based on the non-coincident and coincident measurements of ions.

Identification of different ionization and fragmentation channels

The single pulse measurements described here were carried out using two intensities later used in pump-probe experiments, $\sim 2 \times 10^{14}$ W/cm² and $\sim 4 \times 10^{14}$ W/cm². The time-of-flight (TOF) spectrum of all ions detected after ionization and fragmentation of CH₂I₂ molecules is shown in Fig. 4.1 for these two intensities. This spectrum is determined by the charge-to-mass ratio of ions and, thus, provides an overview of the ionic species produced. The spectrum is dominated by the parent ions (CH₂I₂⁺), singly charged CH₂I⁺ and I⁺ ions, as well as CH_x fragments. Noticeable contributions from different doubly charged ions and molecular iodine ions (I₂⁺) are also present in the spectrum, as well as some background events, either from the residual gas in the chamber (H₂O⁺, O₂⁺ etc.), or from CH₂ICl contamination. The TOF spectra for both intensities have similar fragments present, for higher intensity (red line in Fig. 4.1), the peaks resulting from doubly charged ions are significantly larger, as could be expected. One can also see some rather broad, nearly symmetric structures, like those labeled as I⁺ or I₂⁺. These structures reflect the momentum distribution of the corresponding ionic species along the spectrometer axis (z) which coincides with the laser polarization direction. The central point of such a structure corresponds to the TOF of the ion with zero momentum

along the spectrometer axis, and symmetric structures at shorter and longer TOFs reflect the ions with non-zero momenta emitted in the hemisphere of the detector, or into the opposite one, respectively. It should be noted that in Fig. 4.1 some of these structures overlap with those originating from different species with different mass-to-charge ratio.

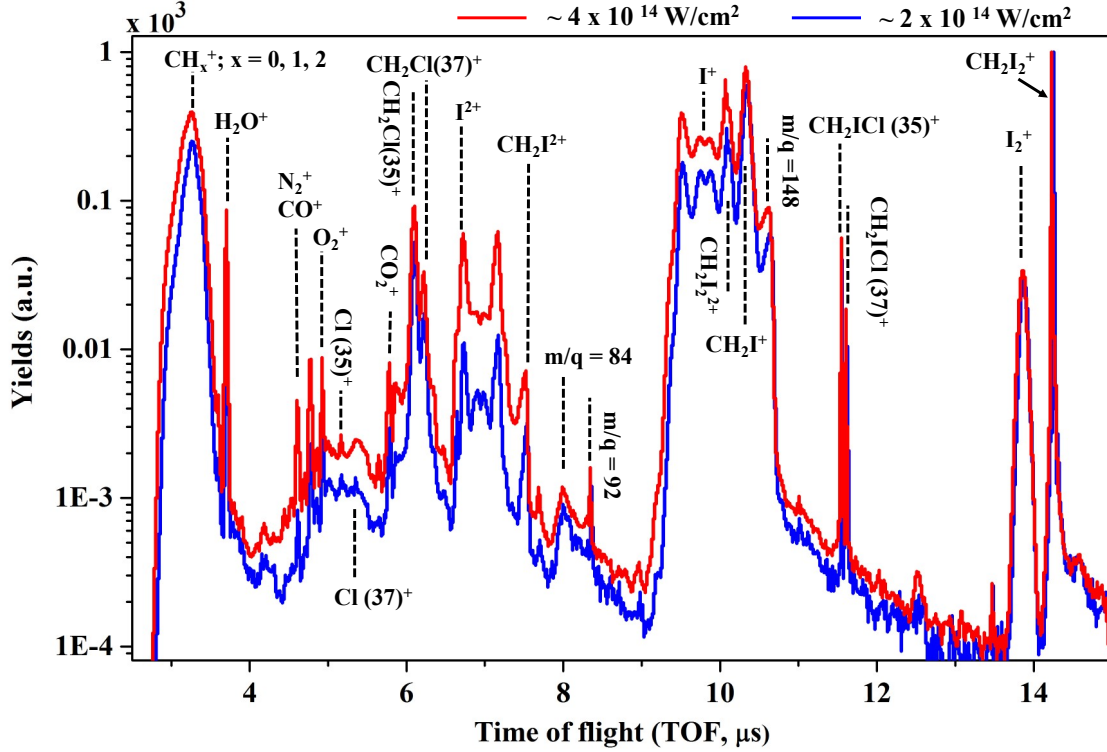


Figure 4.1: Time of flight (TOF) plot of ions after a single NIR pulse. In this plot, TOF values of ions of CH_2I_2 molecule in presence of strong-field are labeled based on their mass-to-charge ratio as indicated by the dashed lines. TOF distributions are normalised to 1 with respect to the parent ion. Blue and red lines correspond to the intensities $\sim 2 \times 10^{14} \text{ W/cm}^2$ and $\sim 4 \times 10^{14} \text{ W/cm}^2$ respectively.

This is further illustrated in Fig. 4.2, where a portion of the TOF spectrum for the lower intensity is shown as a function of the ion hit position on the detector x (along the jet propagation direction). Here, the multi-peak structures seen in Fig. 4.1 (e.g., for the I^+ ions) appear as 2D features like circles, partial circles or coils. These 2D features represent the scaled projections of the 3D momentum distribution for a corresponding species onto the x - z plane, determined by the TOF axis and the jet propagation direction. The ions with low momenta appear in the middle, whereas those with higher momenta end up in the outer region. As can be seen in Fig. 4.2, the high-energy wings of I^+ and CH_2I^+ ions overlap. In

the same region, the contribution from a bound doubly charged parent ion can be seen as a short vertical stripe. It is narrow compared to all other features because its momentum can be balanced only by the sum momenta of the two emitted electrons, which are rather small.

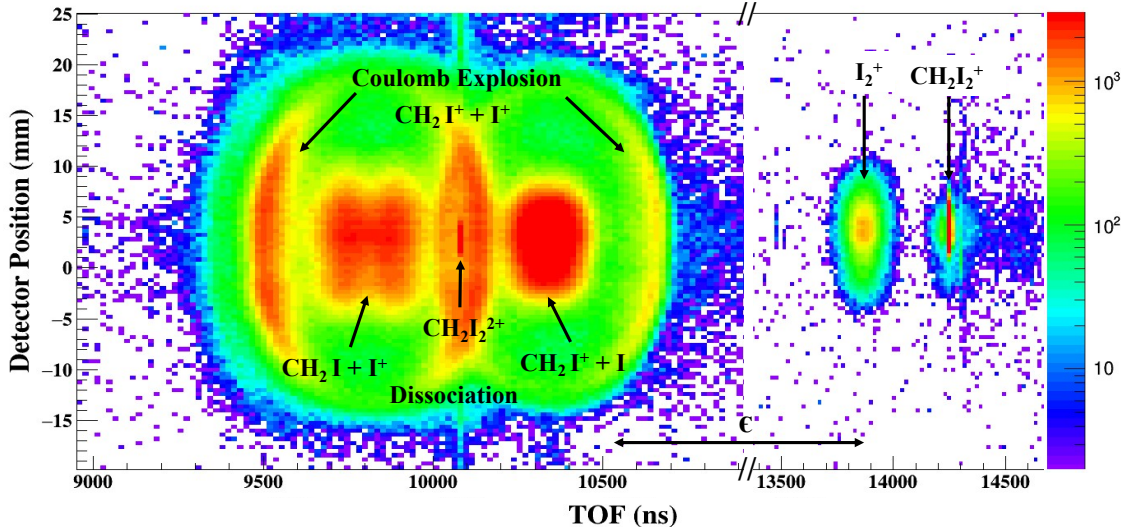


Figure 4.2: Ion time of flight (TOF) spectrum as a function of ion hit position at the detector after the ionization and fragmentation of CH_2I_2 by a single NIR pulse. The spectrum is zoomed into two areas, displaying the TOF regions containing I^+ and CH_2I^+ ions on the left, and I_2^+ and CH_2I_2^+ ions on the right. Fragments resulting from the dissociation of the cation and from the Coulomb explosion of the dication, as well as singly and doubly charged parent ions are labeled in the figure. The intensity of the laser pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$.

The blue line in 4.3 depicts the measured kinetic energy (KE) distributions obtained for four major singly charged species without any coincidence conditions. As can be seen from the figure, all distributions are dominated by a strong low-energy peak, but contain additional higher KE (with the exception of the I_2^+ distribution). The low-energy peaks correspond to the middle regions of the corresponding 2D patterns observed in Fig. 4.2, and mostly reflect the ions resulting from the dissociation of singly charged molecular ions. Correspondingly, they have a neutral partner, and the absence of Coulomb repulsion results in low KE. In contrast, the events originating from the breakup of higher charge states are expected to have higher KE because of the Coulomb repulsion. Although we do not directly detect neutral fragments, this intuitive assignment can be to a large extent verified by analyzing various coincidence channels.

A concept of a coincident measurement for the two-body breakup is illustrated in Fig. 4.4, where the so-called photoion-photoion coincidence (PiPiCo) spectrum is displayed. In this graph, the TOF of the first detected ion is plotted vs. the TOF of the second one. Since, as discussed above, each TOF spectrum reflects the momentum distribution of the corresponding ion, the “true” two-body coincidence events fulfilling momentum conservation appear as narrow diagonal lines. The remaining contributions to this spectrum, appearing as broader or structureless features, originate either from many-body breakup, where one or more fragments is not included in this spectrum, or from “false” (random) coincidence events, which result e.g., from the fragmentation of two different molecules. Filtering on a specific coincidence line, and adding the condition that the two other momentum components (perpendicular to the TOF axis) are also conserved, one can extract events originating from a particular channel. As will be discussed later, such analysis can be readily extended to the three-body fragmentation channels yielding three charged products.

The KE distributions obtained from different two-body (red line) and three-body (black line) fragmentation pathways are plotted on top of the non-coincident (blue) KE distribution of the corresponding ion in Fig. 4.3. One can see that all distinct high-energy features in the non-coincident spectra can be associated with a specific coincident channel. Since all these curves are normalized to 1 at their respective maxima, the relative height of different peaks has no significance, and the fractional contribution of coincidence events to the total spectrum can be coarsely judged simply by the height of the blue, non-coincident curve in the corresponding KE region. Since the data shown in Fig. 4.3 and 4.4 are obtained with the lower of the two used NIR intensities, the fraction of coincident events is rather minor. It significantly increases in the spectra obtained at higher intensities.

From the analysis of Fig. 4.1-4.4, it is clear that at 2×10^{14} W/cm² diiodomethane fragmentation is dominated by single ionization or dissociative ionization resulting in singly charged species. Possible contributing two-body pathways include: (1) $\text{CH}_2\text{I}_2 \rightarrow \text{CH}_2\text{I}^+ + \text{I}$ (the channel requiring least energy, see Table 2.1; (2) $\text{CH}_2\text{I}_2 \rightarrow \text{CH}_2\text{I} + \text{I}^+$; (3) $\text{CH}_2\text{I}_2 \rightarrow \text{CH}_2 + \text{I}_2^+$; (4) $\text{CH}_2\text{I}_2 \rightarrow \text{CH}_2^+ + \text{I}_2$.

Besides that, a significant fraction of bound parent ions is produced. Furthermore, low-

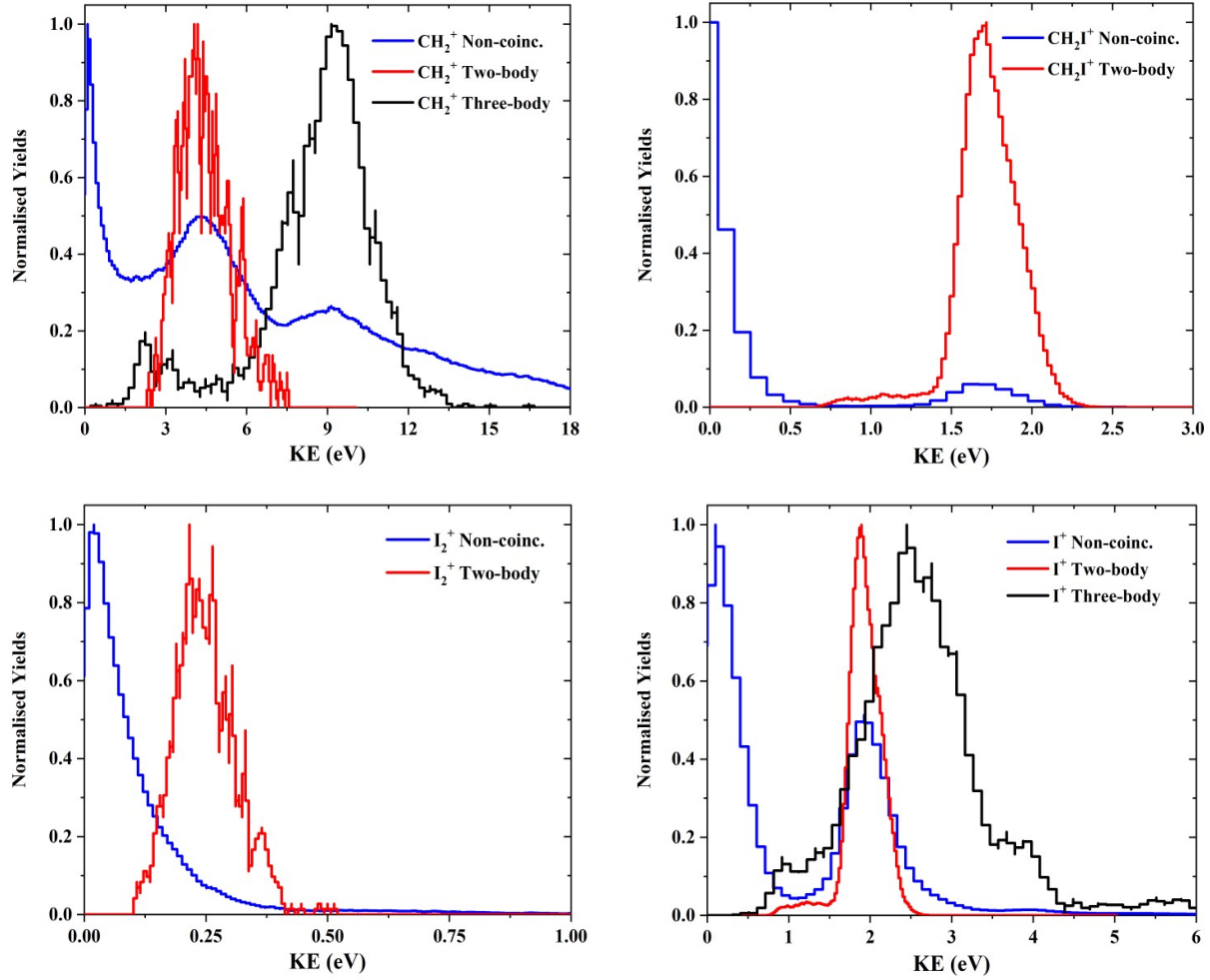


Figure 4.3: Kinetic energy (KE) distributions of fragments of CH_2I_2 molecule after a single NIR pulse. In these 1D plots, the KE distributions of CH_2^+ , I^+ , CH_2I^+ and I_2^+ fragments in final charge states are plotted and are indicated by the blue color. The KE distributions in red and black color represent the distributions of fragments in two- and three-body coincident channels, respectively. The yields of the fragments are normalised to 1 with respect to maximum yield. Intensity of the laser pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$.

energy peaks of I^+ , CH_2^+ and potentially I_2^+ might also contain some contributions from three-body breakup channels, where both partners remain neutral. For two-body channels (1-4) listed above, the KE of the neutral partner and the dissociation KER can be calculated from the KE of the measured ion using the relations 2.6-2.8. For two-body coincident channels, all of these quantities are directly measured, as illustrated for $\text{CH}_2^+\text{I}^+ + \text{I}^+$ and $\text{CH}_2^+ + \text{I}_2^+$ channels in Fig. 4.5. The energy sharing between fragments in this case is determined by the inverse ratio of masses, with the lighter fragments taking most of the available KE. In

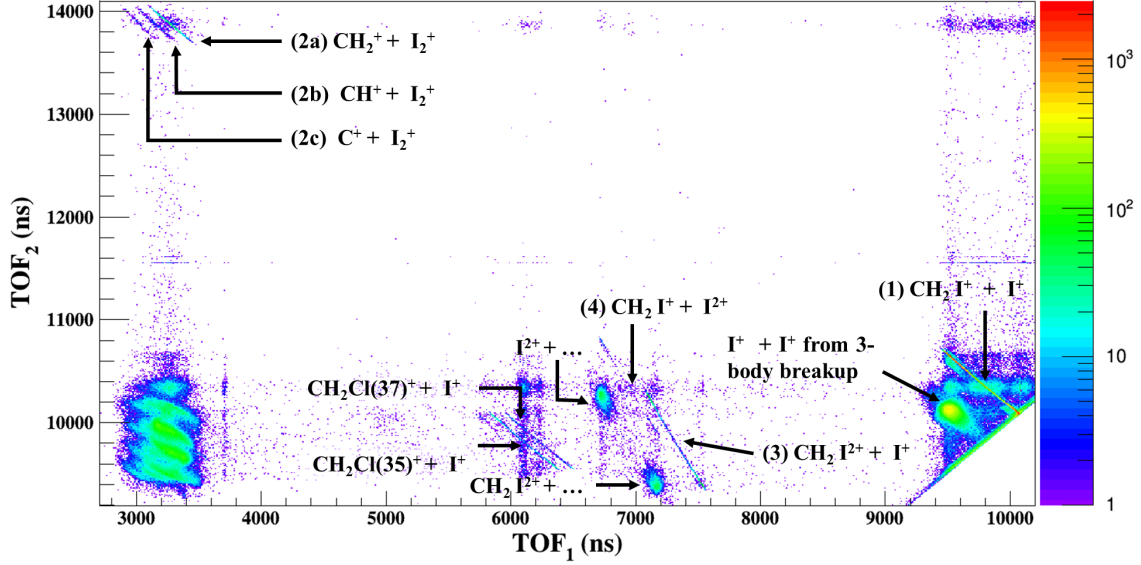


Figure 4.4: Photoion-photoion coincidence (PiPiCo) plot for the fragmentation of CH_2I_2 molecule after a single NIR pulse. In this 2D plot, the time of flight (TOF_1) of a lighter fragment is plotted against the time of flight (TOF_2) of a heavier fragment. The coincident channels are identified as the diagonal lines and are labeled based on their TOF values. Intensity of the laser pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$.

this graph, the experimental data are also compared with the prediction of a simple CE simulation assuming instantaneous double ionization and CE, as described in section 2.5 (see also Fig. 2.18). From Fig. 4.5 it is clear that the CE simulation overestimates the experimental data, although it does fall onto the high-energy tail of the KE distributions for heavy fragments. The outcome of the simulation for CH_2^+ energy and the total KER in the $\text{CH}_2^+ + \text{I}_2^+$ channel overestimates the experimental results even more, and falls outside of the depicted KE range. As discussed in section 2.5, while the overall trend in the simulation is to overestimate the real CE energy, because of the non-Coulombic final state curves and the stretching of the molecule during the pulse, it fails completely for I_2 elimination channel because there, the approximation of a point-like charge localized at the center-of-mass is completely inadequate.

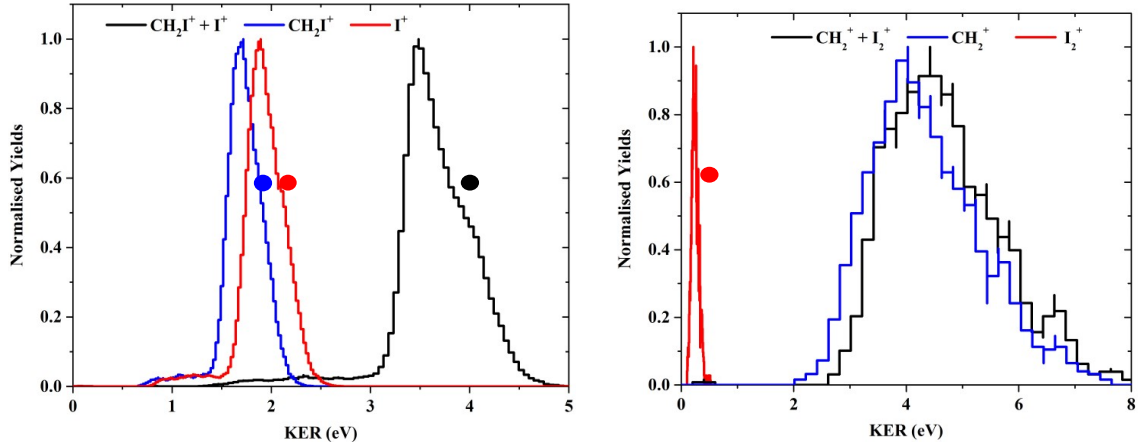


Figure 4.5: Kinetic energy release (KER) distributions of coincident channels after single NIR pulse. In this 1D plot, the KER distributions of $\text{CH}_2\text{I}^+ + \text{I}^+$ and $\text{CH}_2^+ + \text{I}_2^+$ channels are plotted as black lines. The corresponding KE distributions of the individual fragments are shown in red and blue color. The yields of the fragments are normalised to 1 with respect to maximum yield. Solids circles represent the simulated values assuming instantaneous CE starting from the neutral CH_2I_2 geometry. Intensity of the laser pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$.

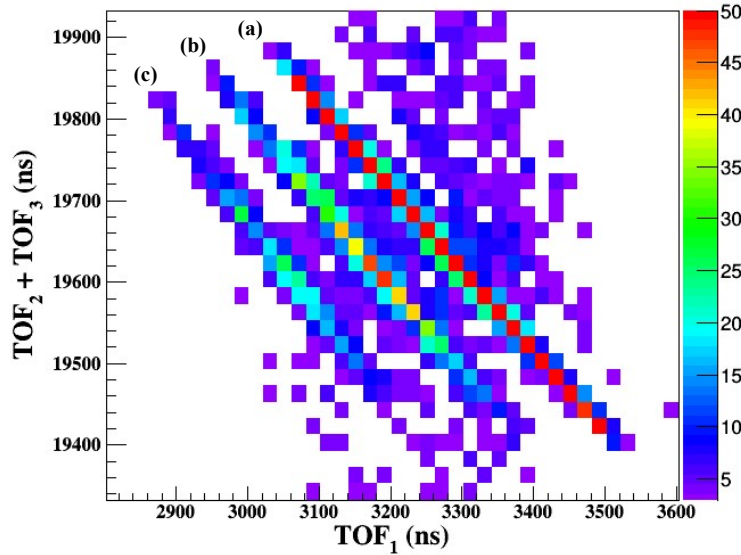


Figure 4.6: Three-particle photoion coincidence plot (sometimes dubbed as “TriPiCo”) for the three-body breakup $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ channel after a single NIR pulse. In this 2D plot, the time of flight (TOF_1) of CH_x^+ ($x = 0, 1$ and 2) is plotted against the sum of time of flight ($\text{TOF}_2 + \text{TOF}_3$) of I^+ fragments. The three-body breakup coincident channels (a), (b), and (c) are labeled based on their TOF information. The channel labeled as (a) is $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ while the channels labeled as (b) and (c) include two I^+ fragments with the CH^+ and C^+ fragments, respectively. Intensity of the laser pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$.

Analysis of three-body breakup and identification of contributions from metastable intermediate configurations

In Fig. 4.6 a concept of ion-ion coincident measurement is extended to the case of a three-body breakup into three charged species. By measuring three ionic fragments in coincidence and plotting the TOF of the first hit vs. the sum of the TOFs of the second and the third ones, one can readily see diagonal lines reflecting momentum conservation, similar to Fig. 4.4. The three lines visible in Fig. 4.6 reflect the three-body molecular breakup into ($\text{CH}_2^+ + \text{I}^+ + \text{I}^+$) channel (line (a)), as well as fragmentation pathways, where the CH_2 group losses one (b) or two (c) hydrogen atoms (channels $\text{CH}^+ + \text{I}^+ + \text{I}^+$ and $\text{C}^+ + \text{I}^+ + \text{I}^+$, respectively). Since the hydrogens are light compared to the other fragments, a missing hydrogen atom hardly results in the deviation from the momentum conservation (except for a slight broadening of the corresponding lines). Nevertheless, in the following analysis, we will ignore those “incomplete” channels, and focus instead on a “complete” three-body pathways like the one depicted by the line (a) in Fig. 4.6.

Several different representation of three-body breakup patterns have been introduced in Section 2.5 (see Fig. 2.15, 2.16 and 2.20). Fig. 4.7 represents one of such maps, the KER of the $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ channel as a function of the angle between the two iodine momentum vectors. The KER distribution, the KE of the individual fragments and the predictions of the CE simulation for each of those observables at the equilibrium distance are shown in the left upper panel of the same graph. As discussed before, the simulated values here again falls into high-energy tail of the experimental energy distributions. The (KER, Θ) distribution contains two distinct features, marked by the dashed ovals, a dominant, tilted structure marked as (1), at 140-150°, and a region marked (2), at somewhat lower KERs, centered at ~ 12 eV and covering the range from 150 to 180°. The dominant island (1) reflects the geometry range expected for the three-body Coulomb explosion of a bound CH_2I_2 molecule. The low-KER region is empty, in contrast to Fig. 2.20, since a single pulse can only explode the bound molecule, with the bond lengths not elongated too much.

To confirm the assignment of the region (1), and to understand the mechanism behind

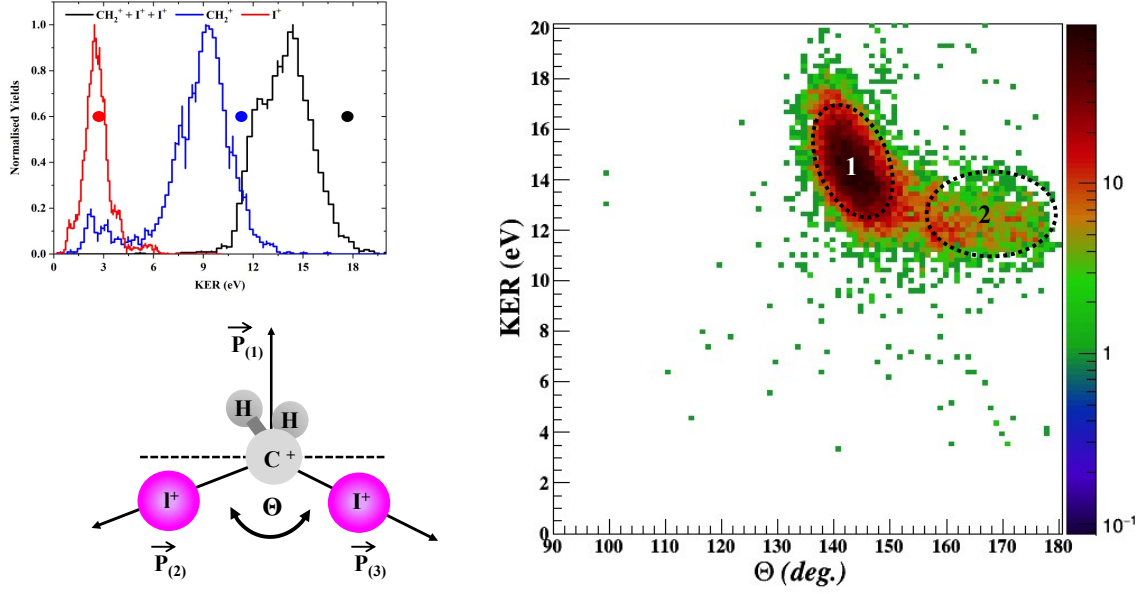


Figure 4.7: KER- Θ plot for the 3-body coincident $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ channel after a single NIR pulse. In this 2D map, the measured yield of the three-body events are plotted as a function of KER values and emission angles. Dashed regions mark the distinct KER- Θ features. The corresponding 1D KER distribution along with the definition of emission angle “ Θ ” are shown on the left of the 2D map. The yields of the fragments are normalised to 1 with respect to maximum yield. Intensity of the laser pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$.

the feature (2) propagating to large angles in Fig. 4.7, we employed the other representations of the three-body breakup discussed in section 2.5: Dalitz plots, Newton diagrams and KE sharing plots. We start with the analysis of the Dalitz plots in Fig. 4.8 (a-c). Fig. 4.8 (a) presents the Dalitz plot for all $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ fragmentation events shown in Fig. 4.7. This graph displays two distinctly different structures: an oval region in the upper part of the plot (marked with a white dashed line), and an X-shaped feature below this oval. In Fig. 4.8 (b) and (c) the same graph is plotted for the regions marked (1) and (2) in Fig. 4.7, respectively. From these graphs it is clear that the region (1) in the (KER, Θ) map of Fig. 4.7 corresponds to the oval feature in the Dalitz plot (Fig. 4.8 (b)), whereas the region (2) is reflected in the X-shaped feature (Fig. 4.8 (c)). These two regions also have very different appearance in the energy sharing diagrams of the two iodine fragments shown in Fig. 4.8 (d-f). There, the events from the region (1) of Fig. 4.7 appear as the dominant half-oval band in the lower left region of the plot, centered at equal energy sharing (see Fig. 4.8 (e)), whereas the events from the region (2) (Fig. 4.8 (f)), are reflected by the cross-like structure marked with

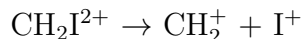
dashed black lines in Fig. 4.8 (d). In both representations shown in Fig. 4.8, the dominant feature formed by the events from the region (1) correspond to the expectations for the concerted fragmentation mechanism, where all three fragments receive considerable fraction of the total energy. Here, the motion of the nuclei in the intermediate ionization states results in a somewhat lower fractional energy of the lighter CH_2^+ fragment compared to the prediction of the instantaneous CE model (cyan circle in Fig. 4.8 (a,d)), whereas asymmetric vibrational modes in the intermediate states can result in unequal energy sharing between the I^+ fragments. The latter is reflected in the horizontal spread of an oval feature away from the central line in the Dalitz plots, and in the off-diagonal broadening of the corresponding feature in the energy sharing diagram (Fig. 4.8 (e)).

As was shown in Ref. [114] [115], a diagonal X-shaped structure in a Dalitz plot can often be a signature of a sequential fragmentation channel producing the metastable intermediate molecular ion, which lives longer than its rotational period. For the specific example of a triply ionized CH_2I_2 molecule, such sequential fragmentation pathway could include the following steps:

Step(1) - breaking of one of the C-I bond and formation of the metastable CH_2I^{2+} intermediate:



Step (2) - decay of the metastable CH_2I^{2+} :



If the rotation of the intermediate occurs in the fragmentation plane, such sequential process results in a breakup pattern, where the energy of one of the two detected iodine ions (emitted in the second step) is correlated with the CH_2^+ energy, whereas the energy of the other iodine is uncorrelated with the energies of the other two fragments. This is reflected in the two diagonal lines that form the X-shaped feature in the Dalitz plots in Fig. 4.8 (a,c). The same process can be identified in the (I^+, I^+) energy sharing diagram shown in Fig. 4.8 (d,f), where the KE of the iodine detached in the first step is uncorrelated with the second one, resulting in vertical and horizontal lines marked in Fig. 4.8 (d) [116].

A more rigorous method to separate concerted and sequential pathways of a three-body

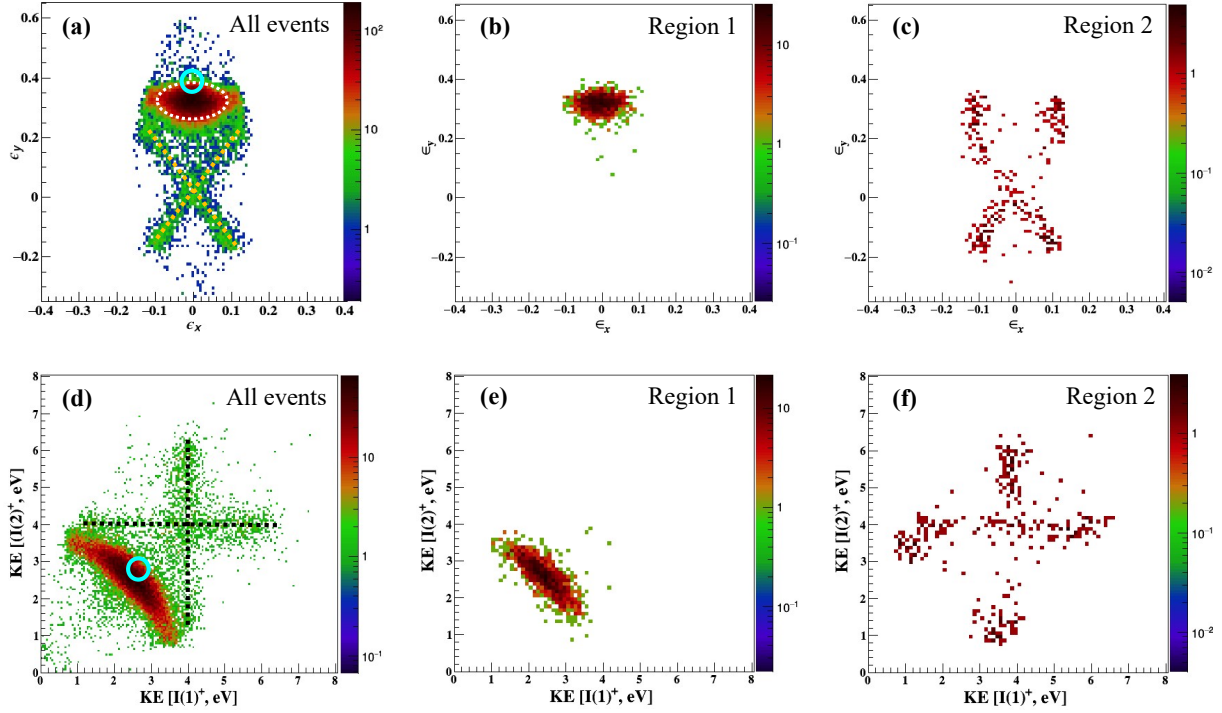


Figure 4.8: (a) Dalitz plot for all events of the $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ coincident channel after a single NIR pulse. The x and y coordinates of this graph is defined as $\epsilon_x = \frac{\epsilon_{\text{I}(1)} - \epsilon_{\text{I}(2)}}{\sqrt{3}}$ and $\epsilon_y = \epsilon_{\text{CH}_2} - \frac{1}{3}$, respectively, where $\epsilon_i = e_i/\text{KER}$ and e_i is the energy carried by the i^{th} fragment after breakup (see section 2.5). White dashed oval indicate the region expected for concerted breakup mechanism. (b): Same as (a) but only for the events from region (1) in Fig. 4.7. (c): Same as (a) and (b) but only for the events from region (2) in Fig. 4.7. (d) KE sharing diagram of coincident I^+ fragments for all events of the $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ coincident channel. (e): Same as (d) but only for the events from region (1) in Fig. 4.7. (f): Same as (d) and (e) but only for the events from region (2) in Fig. 4.7. (d). Cyan circles in (a) and (d) represents the simulated value assuming instantaneous CE starting from the neutral CH_2I_2 geometry.

molecular breakup based on the so-called “native frames” approach has been developed recently [72] [73]. This approach relies on the analysis of the coincident three-body events in the frame of reference associated with each sequential breakup step, and makes use of the rotation of the intermediate molecular fragment [72]. Specifically, the first step is analyzed in the center-of-mass (c.m.) frame of the whole triply charged molecule, and the second step in the c.m. frame of the intermediate dication (like CH_2I^{2+} in the example considered above). If this rotation occurs in the fragmentation plane, the relative direction of the unimolecular dissociation of the dication in the fragmentation plane is expected to be

uniform. As demonstrated in [72] [73], this can be efficiently exploited for the separation of concerted and sequential fragmentation channels, and for the identification of the specific sequential breakup pathway. Corresponding “native frame” analysis of the data shown in Fig. 4.7-4.8 [117] confirmed that the events in region (1) of Fig. 4.8 mainly originate from the concerted $\text{CH}_2\text{I}_2^{3+}$ breakup, whereas region (2) (and also Fig. 4.8 (c,f)) is dominated by the sequential breakup via intermediate CH_2I^{2+} dication. The Dalitz plots and energy sharing diagrams obtained for these concerted and sequential channels separated using “native frames” approach closely resemble the corresponding patterns observed in Fig. 4.8(b,e) and Fig. 4.8(c,f), respectively. The same analysis also suggest that both regions also contain a limited amount of events due to the sequential breakup via I_2^{2+} intermediate [117].

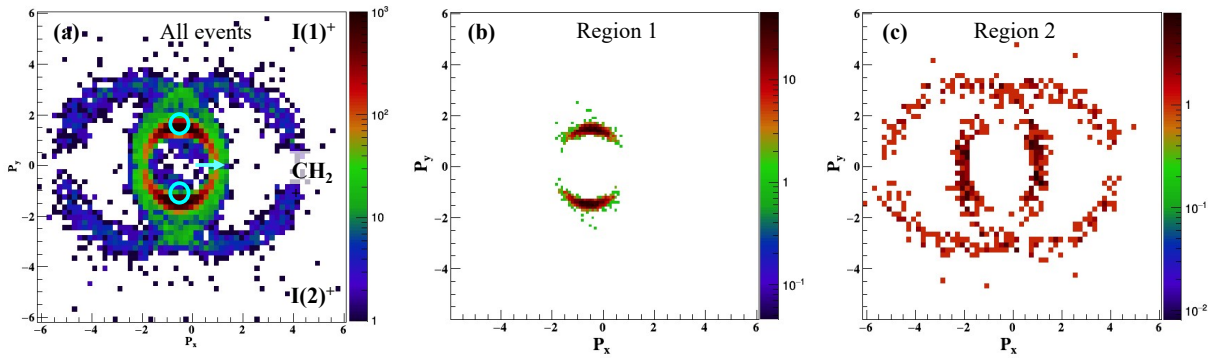


Figure 4.9: (a) Newton plot for all events of the $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ coincident channel after a single NIR pulse. In the 2D plot, the momentum vector of the CH_2^+ is represented by an arrow fixed at one arbitrary unit. In this 2D plot, the momentum vector of the CH_2^+ is represented by an arrow fixed at one arbitrary unit. The momentum vectors of the first and second iodine ions ($\text{I}(1)^+$ and $\text{I}(2)^+$) are normalised to the magnitude of the momentum vector of the CH_2^+ and are mapped in the lower and upper half-plane of the plot. (b): Same as (a) but only for the events from region (1) in Fig. 4.7. (c): Same as (a) and (b) but only for the events from region (2) in Fig. 4.7 (d).

Complementary view of the contribution from intermediate metastable ions can be obtained from the Newton diagrams, as shown in Fig. 4.9. In this representation, as detailed in section 2.5, the momentum vector of the CH_2^+ is represented by an arrow fixed at one arbitrary unit. The momentum vectors of the two I^+ ions are normalized to the magnitude of the CH_2^+ momentum vector. These normalized momentum vectors of the first and the second iodine fragments (ordered by their arrival time on the detector) are plotted in the

lower and upper half-plane of the graph, respectively. In the Newton diagram shown in Fig. 4.9 (a), a “crescent-like” feature in the middle on top of the two overlapping, nearly circular structures on each side can be observed. These structures are well separated in Fig. 4.9 (b) and (c), where only the events from regions (1) and (2) of Fig. 4.7, respectively, are included. The Newton plots obtained after filtering the data using the “native frame” analysis [72] [73] [117] confirms the above-made assignment of these two regions to the concerted and sequential breakup, respectively. The isolated crescent-like feature in Fig. 4.9 (e) reflects the correlated emission of the two iodine ions in the concerted mechanism, whereas two partially overlapping circles in Fig. 4.9 (c) mainly results from the sequential fragmentation mechanism via the CH_2I_2^+ intermediate. Note that in the current representation, with the CH_2^+ momentum vector pointing to the right, the Newton diagrams are symmetric with respect to the horizontal axis because each of the two iodine fragments can equally likely originate from either step of the sequential process.

Three-body breakup patterns for different final charge states

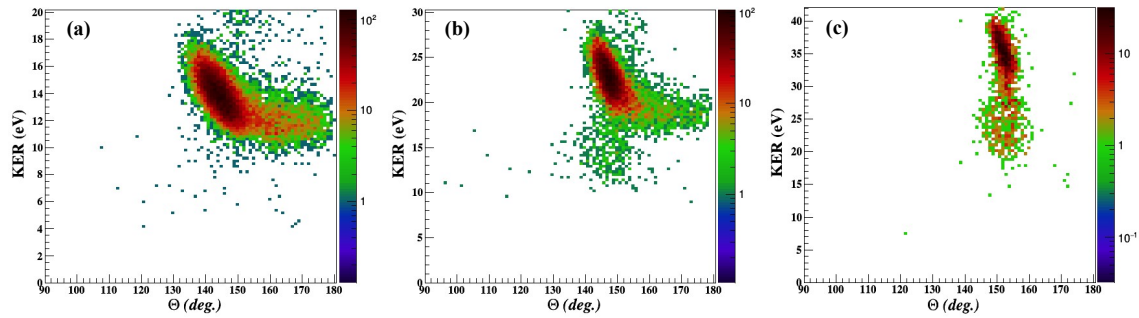


Figure 4.10: KER- Θ plot for the three-body coincident channel in different final charge states after a single NIR pulse. These 2D maps are KER- Θ plots for the coincident channels: (a) $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$, (b) $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^+$, and (c) $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$. Intensity of the laser pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

The sequential fragmentation of long-lived metastable intermediate ions discussed above destroys the concept of CEI of molecular geometry since any information on the initial geometry is lost due to the rotation of the intermediate molecular ion. Correspondingly, certain regions of the parameter space (and, thus, certain geometries) become inaccessible

for CEI. Unfortunately, a comparison of the pattern displayed in Fig. 4.7 and the CE simulation depicted in Fig. 2.15 shows that the region of the (KER, Θ) map, where the contribution from the isomerized CH_2I -I is expected, coincides with the feature from the sequential breakup for $(\text{CH}_2^+, \text{I}^+, \text{I}^+)$ channel. However, it is known that the creation of metastable ions is less likely for higher charge states. Fig. 4.10 displays three (KER, Θ) distributions obtained for three-body breakup of triply, quadruply and five-fold charged states. In this figure, it could be traced that, as expected, the contribution of the sequential pathways covering large angles up to 180 degree becomes lower for $(\text{CH}_2^+, \text{I}^+, \text{I}^{2+})$ channel in (b), and disappears for $(\text{CH}_2^+, \text{I}^{2+}, \text{I}^{2+})$ final state (c). The corresponding Newton plots shown in Fig. 4.11 confirm that the plot for the highest charge states is dominated by the concerted breakup. Thus, this challenge appears to be best suited for studies of isomerization process, which will be discussed in Chapter 5. The graph also manifests a concerted breakup contribution at somewhat lower KER. This feature will be also discussed in Chapter 5.

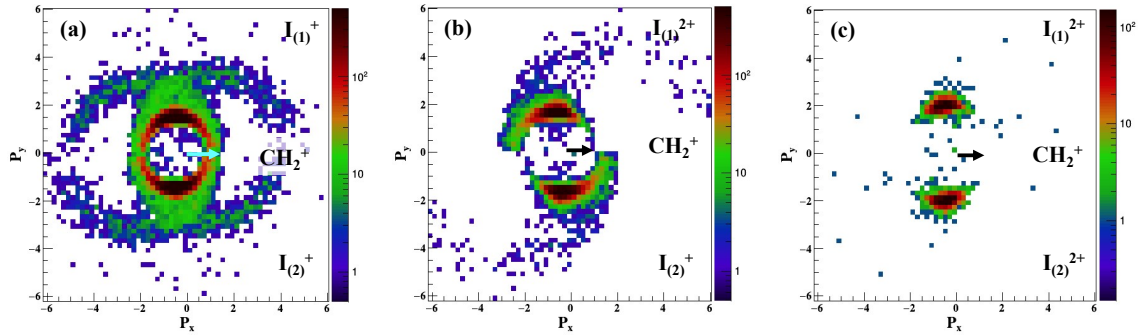


Figure 4.11: Newton Diagram for the three-body coincident channel in different final charge states after a single NIR pulse. These 2D maps are Newton diagrams for the coincident channels: (a) $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$, (b) $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^+$, and (c) $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$. Intensity of the laser pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

4.2 Time-resolved analysis of NIR-driven dynamics in CH_2I_2 probed via two-body breakup

In the previous section, we identified major ionization and fragmentation channels on CH_2I_2 molecules after interaction with a single NIR pulse. In the following, we apply the second

NIR pulse to probe the time evolution of molecular wave packets created by this interaction. The probe pulse can project the wave packet onto one of the variety of higher-lying potential surfaces. This final-state surface, reached after the pump pulse, is thus to a large extent fixed by the selected experimental observable, determined by the combination of particular reaction products observed in the experiment. In this section, we mainly focused on singly-, doubly- and triply-charged states. For all pump-probe experiments presented in this chapter, we kept the pump pulse intensity at $\sim 2 \times 10^{14}$ W/cm², the same intensity as used in Fig. 4.1-4.9. As for the intensity of the probe, its choice depends on the specific goal of the measurement. In general, CEI approach works best if the (multiple) ionization probability is uniform and approaches the probability of 1, i.e., does not depend on the geometry of the molecule. This would strongly favor higher intensities. Practically, however, the limits are set by the background signal, by the contrast of a pump-probe measurement and, for our experimental approach, by the necessity to have less than one event per laser shot. In these experiments, we used the intensity of such “strong” CEI probe of $4\text{-}5 \times 10^{14}$ W/cm². However, for certain aspects of wave packet diagnostics, it is beneficial to employ a weaker probe pulse, such that the probe transition probability becomes geometry-dependent and favors certain configurations, for example, ionic-state resonances, as discussed in section 2.3. Therefore, we have also performed a series of measurements with somewhat weaker probe pulses, set to the same intensity as the pump, i.e., 2×10^{14} W/cm².

Signatures of molecular vibrations in non-coincident ion spectra

Fig. 4.12 depicts the measured (non-coincident) yields of three singly-charged ionic species, the parent ion CH₂I₂⁺ (brown) and two fragment ions: CH₂I⁺ (magenta) and I₂⁺ (green), for two different probe pulse intensities: 4×10^{14} W/cm² (two times higher than the intensity of the pump pulse) in (a) and 2×10^{14} W/cm² (same as the pump pulse) in (b). We observe a substantial enhancement of all ion yields around zero delay, where the two pulses overlap, because of the enhanced effective laser intensity in this region. Besides that, the most pronounced feature for two fragment ion curves is a periodic oscillation with 300 fs periodicity.

This time scale matches the period of “scissors mode” bending vibrations of diiodomethane. The parent ion yields in both panels exhibits a more complicated, rather irregular delay dependence, with what appeared to be a double periodicity. To get more quantitative information on the vibrational frequencies involved, we performed Fast Fourier Transforms (FFTs) of the time-dependent yields shown in Fig. 4.12, and plot the result for each curve in Fig. 4.13 as FFT power spectrum. The spectra for the fragment ions are dominated by a large peak centered at $\sim 110 \text{ cm}^{-1}$, rather close to the scissors mode frequency of the CH_2I_2 ion of 113 cm^{-1} . However, as can be seen from Table 4.1, the corresponding frequency of the neutral ground state differs from this value only by $10\text{-}15 \text{ cm}^{-1}$. Correspondingly, given our FFT error of $\pm 30 \text{ cm}^{-1}$, we cannot reliably discriminate between these two frequencies, as well as between the scissors mode frequencies of different low-lying ionic states. This has been pointed out in a recent transient absorption measurement on NIR-induced dynamics in CH_2I_2 [71]. Since using transient absorption one can discriminate between different electronic states, in that work it was shown that both, ionic and neutral state bending vibrations contribute to the observed oscillation of the signal.

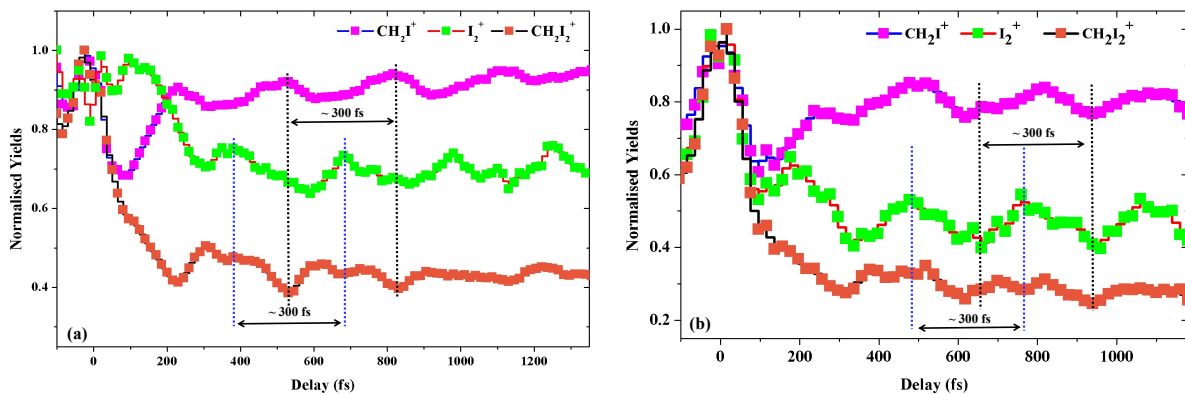


Figure 4.12: Delay-dependent yields of the I_2^+ , CH_2I^+ and CH_2I_2^+ ions integrated over all KEs for: (a) probe intensity $\sim 4 \times 10^{14} \text{ W/cm}^2$ and (b) probe intensity $\sim 2 \times 10^{14} \text{ W/cm}^2$. The yields of the fragments are normalised to 1 with respect to maximum yield and are plotted as a function of the delay between the pump and probe pulses. The ‘0’ in the delay axis marks overlap region of pulses and each delay step is equal to 1 fs. The dashed (black and blue) line marks whether the fragments are in phase or out of phase with each other. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$.

Besides the dominant peak at 110 cm^{-1} , the FFT spectra in Fig. 4.13 contain two

more frequencies. First, there is a contribution centered at 220-225 cm^{-1} , which is most pronounced in the FFTs of the parent ion signal, and is responsible for its double periodicity observed in Fig. 4.12. Second, there is a weak contribution around 500 cm^{-1} in I_2^+ FFT, which is more pronounced in the measurement with the weaker probe pump (bottom row in Fig. 4.13). The latter frequency matches the symmetric stretch frequency of the C-I bond in neutral CH_2I_2 , or that of the asymmetric stretch of the CH_2I_2^+ ion, which nearly coincide. We did not find in literature any vibrational frequency directly matching the 220 cm^{-1} value. Therefore, following the arguments presented in [71], we interpret it as an overtone of the scissors mode frequency.

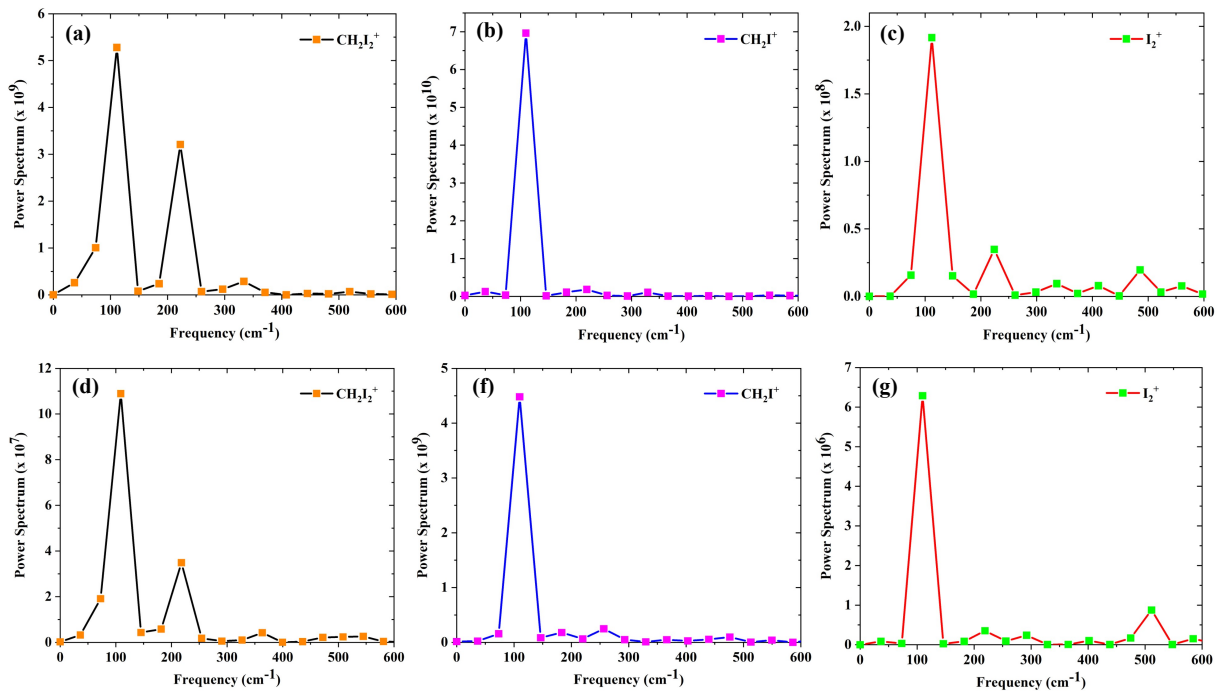


Figure 4.13: Fast Fourier Transforms (FFTs) of the delay-dependent yields of CH_2I^+ , I_2^+ and CH_2I_2^+ ions (integrated over all KEs) for: (a)-(c) probe intensity $\sim 4 \times 10^{14} \text{ W/cm}^2$ and (d) - (f) probe intensity $\sim 2 \times 10^{14} \text{ W/cm}^2$. In this 1D plot, the power spectrum of FFT signals is plotted along the y-axis, while the frequency values are plotted along the x-axis. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$.

Before proceeding with a more detailed discussion of the mechanisms responsible for the appearance of those frequencies, we consider delay-dependent KE distribution of all measured CH_2I^+ ions shown in Fig. 4.14. From this non-coincident spectrum, it is rather clear that there are several different channels contributing to the integrated CH_2I^+ yield shown in Fig.

4.12. Similar to a single-pulse measurement illustrated in Fig. 4.3, the spectrum is dominated by the low-energy CH_2I^+ ions appearing with a neutral iodine partner (red band saturated in color in Fig. 4.14). A pronounced horizontal band between 1.5 eV and 2 eV reflecting the doubly-charged final state $\text{CH}_2\text{I}^+ + \text{I}^+$ can also be observed, with its wings reaching out up to 3 eV KE. Between these two bands, there is a pronounced oscillatory structure, most likely corresponding to high-energy tail of lowest horizontal band, and a descending line propagating towards smaller KE at larger delays. This feature originate from the events, where the pump pulse dissociates the molecule, and the probe pulse results in its CE at the internuclear separations increasing with the delay and will be discussed later. Here, we first focus on the analysis of the vibrational motion.

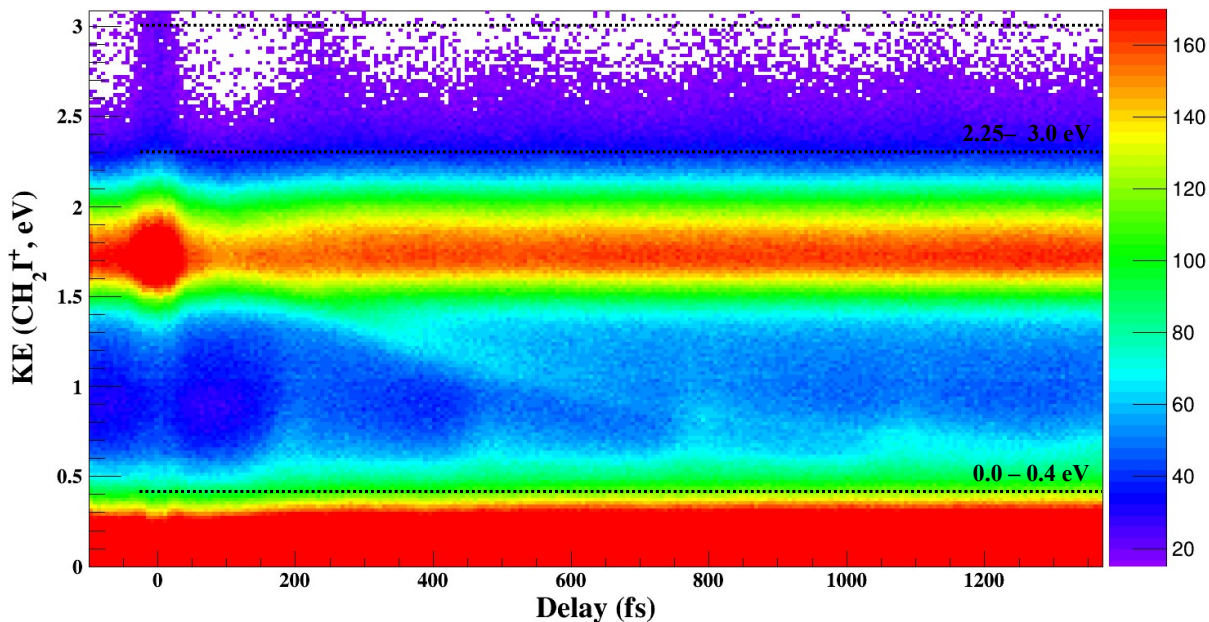


Figure 4.14: Delay-dependent KE distribution of non-coincident CH_2I^+ fragments. The KE distribution of CH_2I^+ fragments is plotted with respect to the delay between the pump and probe pulses. The black dashed lines indicate low KE (0 - 0.4 eV) region and high KE (2.25 - 3.0 eV) regions. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

In order to visualize the signal modulation with time, in Fig. 4.15(a) we plot the projections of the high and low KE regions marked in Fig. 4.14 onto the delay axis. Besides rather complex behavior around zero delay, which can be caused by the depletion effects or by partial saturation of our data acquisition system for the situation, where both pulses

overlap, in both curves, we see a pronounced oscillation with the same 300 fs periodicity as in Fig. 4.12, which is in phase for both KE ranges. The FFT of these delay-dependent yields are plotted in Fig. 4.15(b), showing the dominant frequency at $\sim 110 \text{ cm}^{-1}$, and a clear contribution of the overtone. The first clear maximum of the oscillation appears around 250 fs. All these observations support the picture proposed in [69], where scissors mode vibration in the ground state of the ion and a resonant transition to a dissociative state at the outer turning point of this vibration was suggested as a mechanism responsible for the oscillation of the CH_2I^+ ion yield. The cartoon illustrating this scenario in terms of the PEC plotted as a function of I-C-I bending angle is shown in Fig. 4.16. Since in the ionic geometry the I-C-I angle is smaller, the ionic-state bending vibrations proceeds “inwards” upon ionization. Thus, slightly less than a full cycle is needed for the wave packet to reach the outer turning point, where it can undergo one-photon dissociative transition (hence the first maximum at $\sim 250 \text{ fs}$ for 300 fs period). The same oscillating wave packet can be also projected onto the CE final state curve, reflected in the high-energy band in Fig. 4.14. The increased CE yield at the outer turning point is then due to the lower vertical ionization potential of the ion, as compared to the inner region (smaller I-C-I angles).

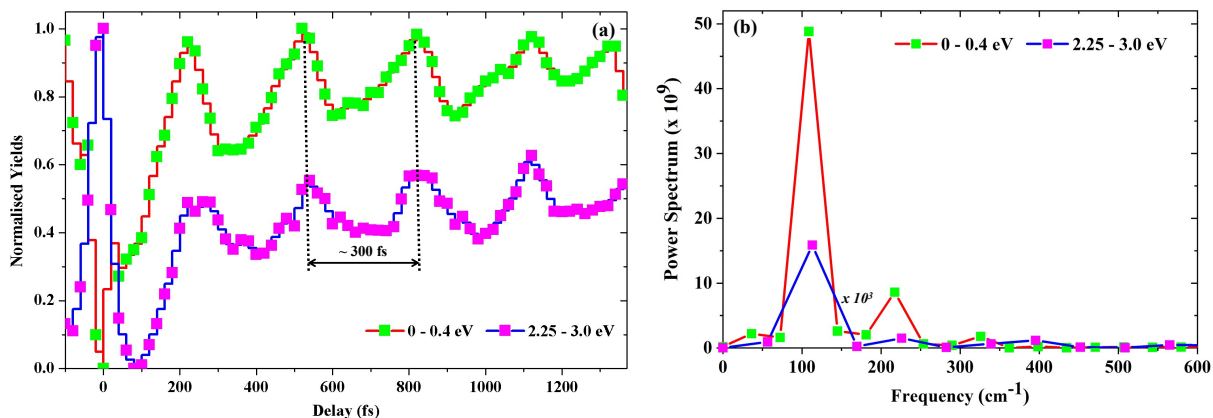


Figure 4.15: (a) Projection of CH_2I^+ fragments in the low KE (0 - 0.4 eV) region and high KE (2.25 - 3.0 eV) region. In this 1D plot, the yields of the fragments are normalised to 1 with respect to maximum yield, and (b) FFT of CH_2I^+ fragments in singly charged final states in the low KE (0 - 0.4 eV) region and high KE (2.25 - 3.0 eV) region. The power spectrum of FFT signals is plotted along the y-axis, while the frequency values are plotted along the x-axis. Intensity of the pump pulse is kept $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

Within this picture, in [69] it was proposed that the elimination of I_2^+ should favor the inner turning point of the bending vibration and, thus, in such pump-probe experiments I_2^+ yield should be out of phase with the CH_2I^+ signal. This is consistent with our observations in Fig. 4.12(a) (for stronger probe pulses), where the maxima of the I_2^+ yield appear close to 400 fs, 700 fs, etc.. In order to confirm the out of phase behavior of the I_2^+ ion signal, we plot the delay-dependent I_2^+ KE in Fig. 4.17(a), and present the projection of the low-energy part of this distribution on the delay axis in Fig. 4.18(a), thus, selecting the yield of the $\text{I}_2^+ + \text{CH}_2^+$ channel. The oscillating (green) curve in Fig. 4.18(a) exhibits pronounced maxima around 400 fs, 700 fs, 100 fs, confirming the phase shift of $\sim \pi$ with respect to the CH_2I^+ signal.

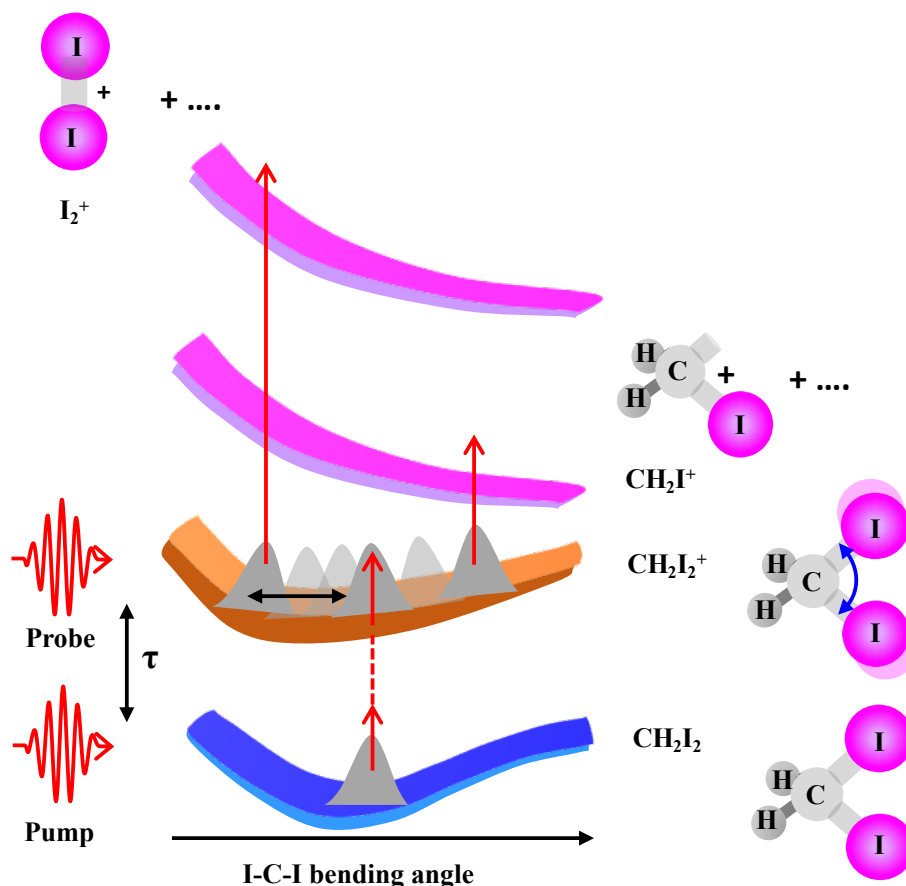


Figure 4.16: Cartoon illustrating the vibrational wavepacket motion along the I-C-I bending coordinate in the CH_2I_2^+ ionic ground state and the CH_2I^+ and I_2^+ formation.

However, the phase relation between these two curves is different when a weaker probe

pulse is used, as can be seen in Fig. 4.12(b). There, the I_2^+ and CH_2I^+ signals oscillate nearly in phase. Interestingly, it is the I_2^+ yield that changes its absolute phase by nearly π compared to Fig. 4.12(a). It is rather surprising since it is natural to expect more efficient I_2 bond formation at smaller I-C-I angles. To understand this counterintuitive behavior, we should realize that the ionization by the pump and subsequent dissociation by the probe discussed above is not the only mechanism for I_2^+ elimination. As evidenced by our single-pulse measurement illustrated in Fig. 4.1-4.3, it also can be efficiently triggered by a single pulse at $2 \times 10^{14} \text{ W/cm}^2$, which is the intensity of our pump pulses and of the “weaker” probe pulse used in Fig. 4.12(b). Since from earlier work [71] we know that we also excite scissors mode vibrations with nearly the same period in a neutral diiodomethane molecule, we interpret the difference in the phase relation between the two fragment ions observed in Fig. 4.12(a) and (b) as the signature of such neutral-state vibrations. In [71], it was shown that the so-called bond softening mechanism is responsible for the vibrational excitation in the neutral CH_2I_2 . In this scenario, sketched in Fig. 4.19, the wave packet in the ground state of the neutral molecule first moves outwards, and needs somewhat less than a full cycle to reach the inner turning point, where it is more likely to form the new (I, I) bond. There, it undergoes dissociative ionization transition induced by the probe ending up on the $\text{CH}_2 + \text{I}_2^+$ repulsive surface. This picture is consistent with the maxima of I_2^+ signal in Fig. 4.12(b) appearing at 200 fs, 500 fs, etc.

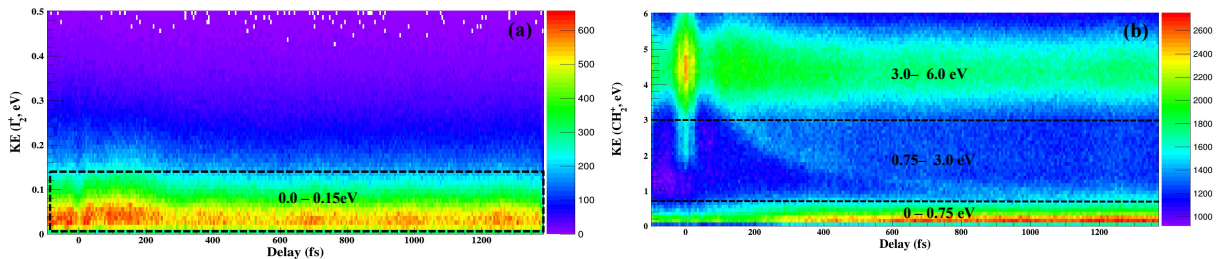


Figure 4.17: Delay-dependent KE distribution of non-coincident I_2^+ (a) and CH_2I^+ (b). Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

The hypothesis of bending vibrations of the neutral being the reason for different phase relation between I_2^+ and CH_2I^+ signals is also indirectly supported by the disappearance, of

the overtone frequency and a cleaner signature of stretching vibrations at $\sim 500 \text{ cm}^{-1}$ for the weaker probe pulse. It is based on the transient absorption spectra presented in Ref. [71], which demonstrate that the overtone feature is associated with the signal from the ions, whereas the stretching frequency appeared at the energies typical for the neutral molecule. Although the exact reason why this scenario becomes more important for a weaker probe pulse is not clear, we argue that, as discussed earlier in this section, the weaker probe pulse is more sensitive to rather small changes in geometry occurring upon vibrational excitation of the neutral molecule.

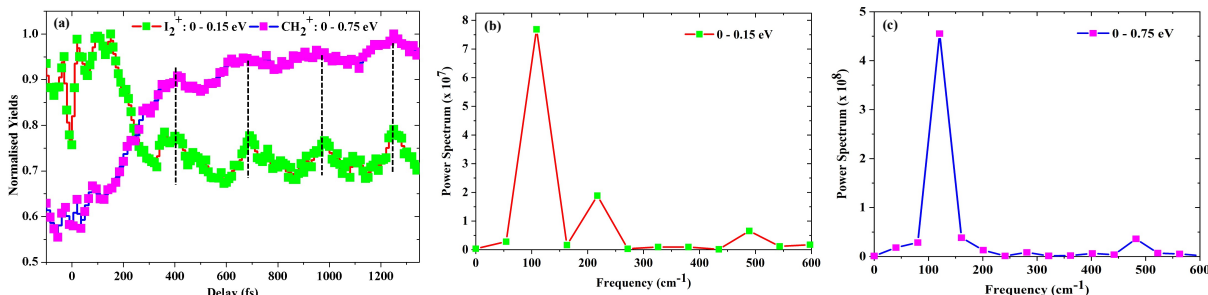


Figure 4.18: (a) Delay-dependent yields of low-energy non-coincident I_2^+ and CH_2^+ fragments. Here, the yields of the low KE fragments shown in Fig. 4.17 (0 - 0.15 eV for I_2^+ and 0 - 0.75 eV for CH_2^+) are projected onto the delay axis. In this 1D plot, the yields of the fragments are normalised to 1 with respect to maximum yield. (b) FFT of I_2^+ fragments in the low KE (0 - 0.15 eV) region, and (c) FFT of CH_2^+ fragments in the low KE (0 - 0.75 eV) region. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

Two scenarios discussed above should also effect the delay dependence of the parent ion yield. In general, the oscillation in the yield of the parent ion can have two apparent underlying reasons: (1) vibrations in the neutral molecule and geometry-dependent probability of subsequent ionization and (2) the depletion of the parent ion signal by fragmentation or further ionization. Strong overtone peak in the FFTs of the parent ion signal does indicate that the depletion plays an important role, since the overtone is not expected for the vibrational excitation of the neutral CH_2I_2 [71]. The depletion process and its delay dependence can be quite complicated since it can be caused by any of the channels ending up in the higher-lying states. For the data shown in Fig. 4.12(a), where two fragment ion yields oscillate out of phase, the depletion could be expected for both, the inner and the outer turning points,

i.e., twice per cycle (note that the next most abundant channel, low-energy I^+ production, which is not shown here, exhibits roughly the same delay dependence as the CH_2I^+ signal). Indeed, a local minimum (a small dip) can be seen in the parent ion signal for each delay, where either of the other two curves has a maximum. Although it is hard to trace the phase change of the parent ion curve between Fig. 4.12(a) and (b), i.e., for stronger and weaker probe pulse, an increased importance of the neutral-state vibrations for a weaker pulse is likely reflected in the position of the first maximum of the curve: while in (a) there is a clear maximum for the parent ion signal at ~ 300 fs, in (b) there is a clear minimum at the same delay. This is also supported by the decrease of the overtone peak in the FFT of the parent ion yield for the weaker probe (see Fig. 4.13(a) and (d)).

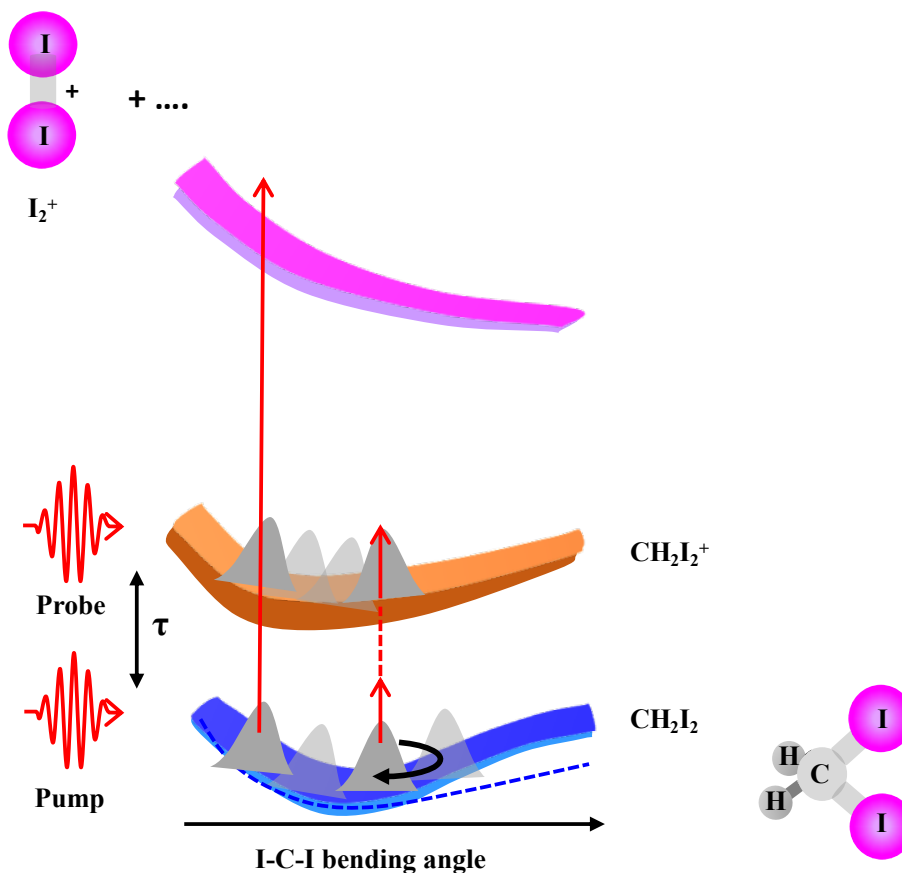


Figure 4.19: Cartoon illustrating the bond softening mechanism in the neutral ground state and vibrational wavepacket motion along the I-C-I bending coordinate in the CH_2I_2^+ ionic ground state and hence, I_2^+ formation.

So far we have discussed the elimination of molecular halogen in the cationic state, where

we can directly detect it as a product (in this case, I_2^+). However, dissociative ionization of CH_2I_2 can also lead to a formation of a neutral I_2 , accompanied by a charged CH_2^+ partner. Since we cannot detect a neutral fragment, we explore a potential contribution of this channel in CH_2^+ spectra shown in Fig. 4.17(b) and Fig. 4.18(a),(c). The delay-dependent KE distribution of CH_2^+ ions shown in Fig. 4.17(b) manifest three features largely similar to those discussed in Fig. 4.14: a dominant low-energy band, a horizontal high-energy band resulting from two-body CE, and a descending band reflecting the CE explosion of dissociating molecules. Since we are interested in a channel involving a neutral partner, we focus on the low-energy band, and plot its projection on the delay axis in Fig. 4.18(a) and the FFT of this projected yield in Fig. 4.18(c). The data in these figures show that the low-energy CH_2^+ yield oscillates with approximately the same frequency corresponding to scissors mode vibrations, and this oscillation is in phase with the low-energy I_2^+ signal also shown in Fig. 4.18(a). Since we used the stronger of our probe pulses here, (4×10^{14} W/cm²), we assume, in accordance with the above discussion, that the maxima of the I_2 curves in this case correspond to the times where the wave packet is at its inner turning point. The only two channels that can produce CH_2^+ ions with such low energies are (1) neutral I_2 elimination and (2) three-body breakup yielding two neutral iodine fragments. Although we cannot reliably discriminate between these two possibilities based on the data, pronounced correlation with bending vibrations and the enhancement of the signal at the inner turning point does suggest that this channel includes contributions from neutral I_2 formation.

Mapping bound and dissociating nuclear wave packets via two-body coincident measurements

After considering non-coincident observables and focusing mainly on the analysis of singly-charged final state, we now focus on the analysis of higher charged states, starting with the pathways producing two charged particles. Besides additional information on the wave packet motion in bound states discussed above, a pump-probe experiment utilizing such

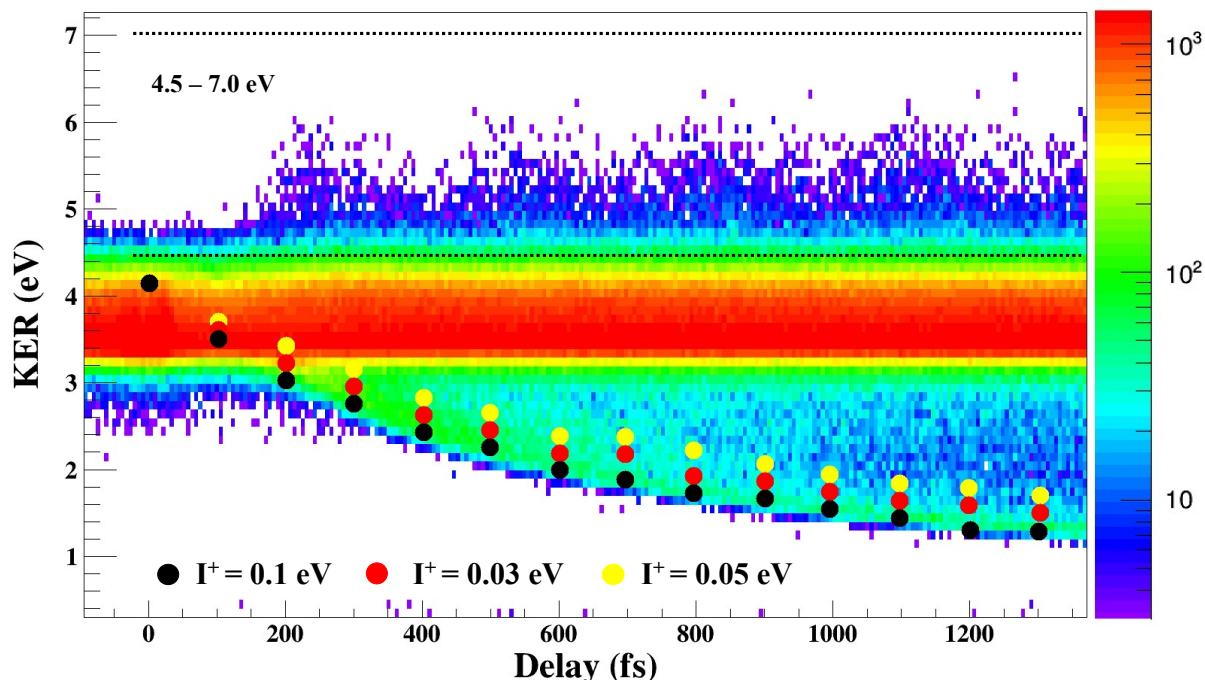


Figure 4.20: Delay-dependent KER distribution for the two-body $\text{CH}_2\text{I}^+ + \text{I}^+$ coincident channel. In this 2D plot, the KER of the $\text{CH}_2\text{I}^+ + \text{I}^+$ coincident channel is plotted as a function of delay between pump and probe pulses. Solid circles represent the simulated KER values at different delays assuming different asymptotic dissociation energies as indicated in the figure. The dashed lines separate the 4.5 - 7.5 eV KER region. Intensity of the pump pulse is kept $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

coincident CE as a probe can efficiently map the dissociation processes triggered by the pump pulse. This is demonstrated in Fig. 4.20, where the measured KER of CH_2I^+ and I^+ coincident pairs is shown as a function of the delay. Three distinct features can be distinguished in this spectrum: (1) an intense horizontal band centered at $\sim 3.5 \text{ eV}$; (2) an oscillatory structure above 4.5 eV; and (3) a pronounced descending band approaching 1 eV at large delays. Band (1) coincide in energy with the single-pulse spectrum for the same channel shown in Fig. 4.5 for the same channel and reflects the CE of a bound molecule, either by a single pulse (the pump or the probe), or by a stepwise sequential ionization, where the first electron is removed by the pump, and the second – by the probe. Neutral or cationic vibrational dynamics discussed above can both contribute to this band, but their signatures are largely covered by intense single-pulse background, especially from the more

intense probe. However, since the ground-state cationic geometry is overall somewhat tighter than the geometry of the neutral (in particular, the I-I distance is shorter), the CE energy for the ionic state is expected to be somewhat higher. CE simulation assuming instantaneous geometry predicts the KER of 4.15 eV (see the black point at 0 delay) for the neutral and 4.67 eV for the ion. Although such simple simulation always tends to overestimate experimentally measured energies, as is clearly the case for band (1) in this figure, the appearance of the oscillatory structure (2) at high KE most likely reflects this shift and, thus results from the high-energy tail of the CE of CH_2I_2^+ cation by the probe pulse. The time offset for the appearance of this structure (120 fs) can be understood as the time needed for the wave packet to adapt to the new, cationic geometry and is, thus, comparable with the half of the bending vibration period. Positions of the maxima and minima appearing in this band can be traced in the projection on the delay axis shown in Fig. 4.21 (a), and match the delays for maxima and minima of the CH_2I^+ signals plotted in Fig. 4.12 and 4.15. The FFT of this projection shown in Fig. 4.21 (b) manifest the same frequency of $\sim 110 \text{ cm}^{-1}$ as the FFTs discussed in the previous sub-section for singly-charged states.

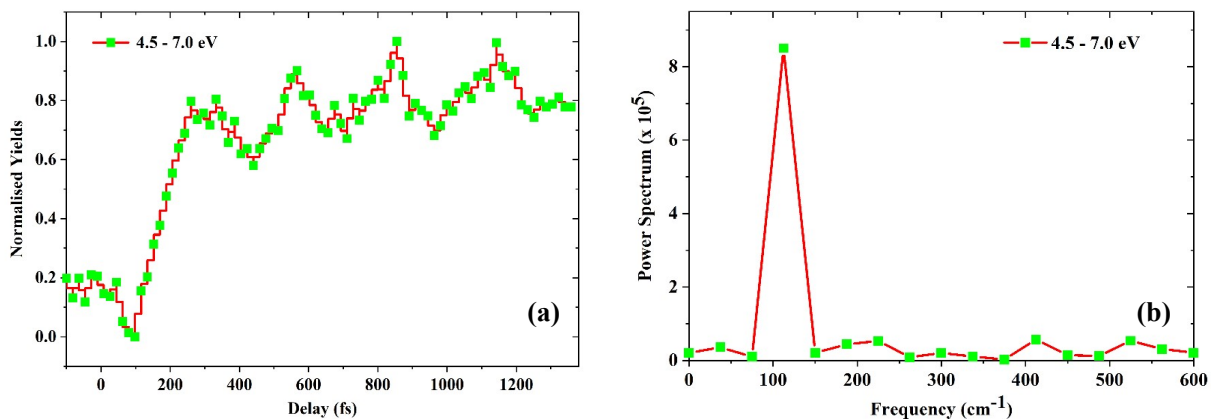


Figure 4.21: (a) Projection of two-body $\text{CH}_2\text{I}^+ + \text{I}^+$ coincident channel in high KER region. The coincident CH_2I^+ and I^+ yields in the 4.0 - 7.0 eV KER region is projected along the delay axis. In this 1D plot, the yields of the fragments are normalised to 1 with respect to maximum yield. (b) FFT of two-body $\text{CH}_2\text{I}^+ + \text{I}^+$ coincident yields in high KER region. FFT is performed on the coincident CH_2I^+ and I^+ yields in the high KER (4.5 - 7.0 eV) region. The power spectrum of FFT signals is plotted along the y-axis, while the frequency values are plotted along the x-axis. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

The descending band (3) reflects the motion of the dissociating wave packet launched by the pump pulse and Coulomb exploded by the probe at increasing internuclear separations, resulting in CE energies and, thus, in the KER decreasing as a function of the delay. While from the final state we can uniquely determine that the molecule dissociates into CH_2I and I fragments, we cannot unambiguously identify the charge state of each partner in the intermediate dissociating state, which can be either 0 or 1 for either partner. However, if both fragments are charged after the pump pulse, the event would appear within the high-energy band and would not fall into the descending structure (3). Therefore, the channels potentially contributing to this structure are $\text{CH}_2\text{I}^+ + \text{I}$, $\text{CH}_2\text{I} + \text{I}^+$ and, potentially, $\text{CH}_2\text{I} + \text{I}$. We cannot differentiate between these channels from the graph in Fig. 4.20 unless we have some additional information on the channel, like its asymptotic dissociation energy, specific angular distribution etc. Although we cannot exclude the contributions from the neutral dissociation channels, it is not a common type of process in strong NIR fields, and, to the best of our knowledge, has not been reported for halomethanes despite numerous strong-field studies. This is in stark contrast to the UV regime, where, as discussed in section 2.2, dissociation into two neutral products is a dominant pathway.

Based on single-pulse spectra presented in Fig. 4.1 - 4.3, both $\text{CH}_2\text{I}^+ + \text{I}$ and $\text{CH}_2\text{I} + \text{I}^+$ dissociative channels are efficiently triggered by our pump pulse. To model these channels, we employ the “instantaneous” CE simulation discussed in section 2.5, with asymptotic dissociation energies estimated using single-pulse data shown in Fig. 4.3. Note that the simulation also does not distinguish between these two dissociative ionization channels mentioned above, such that the iodine energy used in the simulation and denoted as I^+ in the figure, is just a measure of the asymptotic energy and can be associated with either I^+ or neutral I atom. The curve that fits best the main descending band correspond to the iodine asymptotic energy of 0.1 eV, in accordance with the dominance of low-energy CH_2I^+ and I^+ in the results of Fig. 4.3. However, the region above this feature but below the horizontal CE band also contains a non-negligible number of events, indicating that even slower dissociation pathways contribute to the spectrum formation.

Similar dynamics can be explored via the analysis of higher charge states. An example for

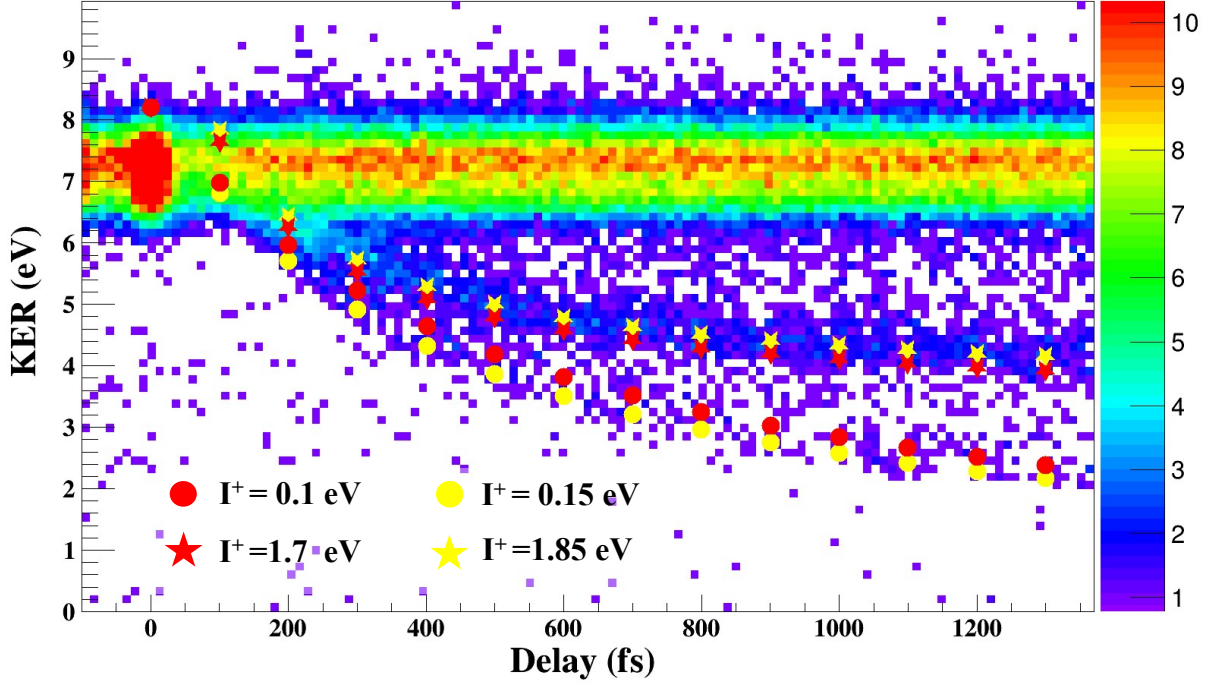


Figure 4.22: Delay-dependent KER distribution for the two-body $\text{CH}_2\text{I}^{2+} + \text{I}^+$ coincident channel. In this 2D plot, the KER of the $\text{CH}_2\text{I}^{2+} + \text{I}^+$ coincident channel is plotted as a function of delay between the pump and probe pulses. Colored symbols represent the simulated KER values at different delays assuming different asymptotic dissociation energies as indicated in the figure. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

such analysis is illustrated in Fig. 4.22, where a delay-dependent KER spectrum is plotted for $\text{CH}_2\text{I}^{2+} + \text{I}^+$ final state. The spectrum exhibits all the features discussed above for the doubly charged channel, but the descending structure here is split into two bands. The lower one reflects the same pathways as the descending band in Fig. 4.20, and can be modeled with the same dissociation energies and double Coulomb repulsion. The additional band converges towards 3-4 eV region at large delays, and reflects the events where two-body CE happens already in the pump pulse. Since we are considering a higher-lying final state, now this channel also exhibit a clear delay dependence, and at large delays converges towards $\text{CH}_2\text{I}^+ + \text{I}^+$ KER, same as the one obtained in single-pulse measurements (Fig. 4.5), or in the horizontal band in Fig. 4.20.

Finally, we consider the two-body CE explosion channel reflecting I_2 or I_2^+ formation in Fig. 4.23. in this graph, the KER for the $\text{CH}_2^+ + \text{I}_2^+$ CE channel is plotted as a function of

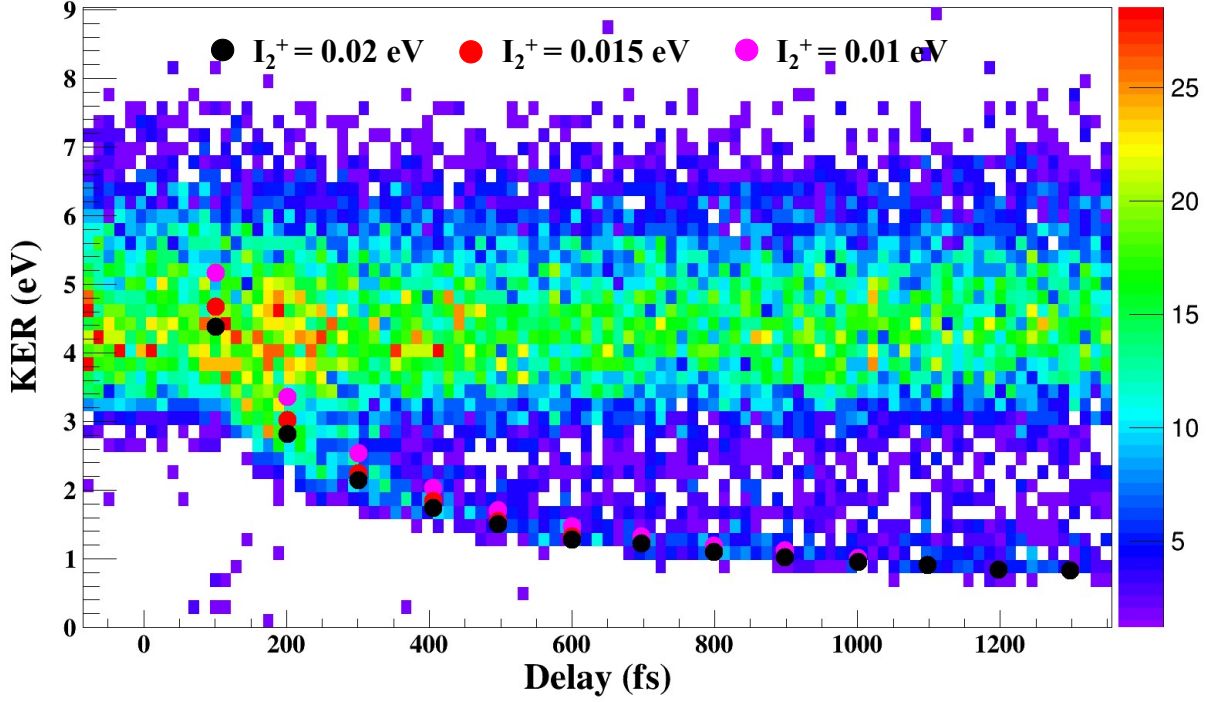


Figure 4.23: Delay-dependent KER distribution for the two-body $\text{CH}_2^+ + \text{I}_2^+$ coincident channel. In this 2D plot, the KER of the $\text{CH}_2^+ + \text{I}_2^+$ coincident channel is plotted as a function of delay between the pump and probe pulses. Solid circles represent the simulated KER values at different delays assuming different asymptotic dissociation energies as indicated in the figure. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

the delay. The spectrum has similar overall structure as the graph in Fig. 4.20 for $\text{CH}_2\text{I}^+ + \text{I}^+$, but with somewhat broader horizontal band. The descending band reflects I_2 or I_2^+ elimination after the pump. Even though it overlaps with the horizontal CE band at small delays, the curve can be traced down to ~ 100 fs delays, providing evidence for direct, “synchronous” I_2 or I_2^+ ejection within first half of bending vibration period after ionization by the pump pulse. Similar to the data for other channels discussed above, this descending curve can be simulated using simple CE model, assuming rather low asymptotic dissociation energies.

4.3 Imaging transient molecular geometries with three-body Coulomb explosion

Experimental approach used in the previous section can provide information about the internuclear separation between two constituents of the molecule and allows for the retrieval of the spatial orientation of the breakup axis within the limits of axial recoil approximation. However, since momentum conservation always forces the fragments resulting from two-body breakup to go back to back, it does not provide direct information on the geometry of a polyatomic molecule. Such information can be obtained from coincident three-body breakup patterns as described at the end of section 4.1. Here, we will apply this technique and all the three-body analysis tool described in section 4.1 for “static” single-pulse experiments, as a probe of strong-field induced molecular dynamics. This work mainly focuses on elucidating and imaging molecular halogen formation, I_2 or I_2^+ , the reaction that necessarily involves the breakage of two molecular bonds and the formation of a new one. In all of the experiments described in this section, we use the same pump-probe configuration as was used for most of the measurements described in section 4.2: 25 fs, 800 nm pump with the intensity of 2×10^{14} W/cm², and more intense, 4×10^{14} W/cm² probe of the same wavelength and duration.

Overview of delay-dependent three-body breakup patterns

In this section, we focus on the final state of the reaction resulting in three singly charged ionic fragments, $CH_2^+ + I^+ + I^+$. The 3D momentum vectors of all three ions are measured as a function of the delay. Molecular fragmentation channels after the pump pulse that contribute to the measured signal include all pathways we discussed in section 4.1. However, as can be seen from Fig. 4.1 - 4.4, even though there is a noticeable contribution of doubly charged ions or even higher charge states, the products of such interaction contain predominantly singly charged fragments. Accordingly, the dominant intermediate channels we should have in mind when analyzing three-body breakup patterns are (1) parent ions $CH_2I_2^+$; dissociative

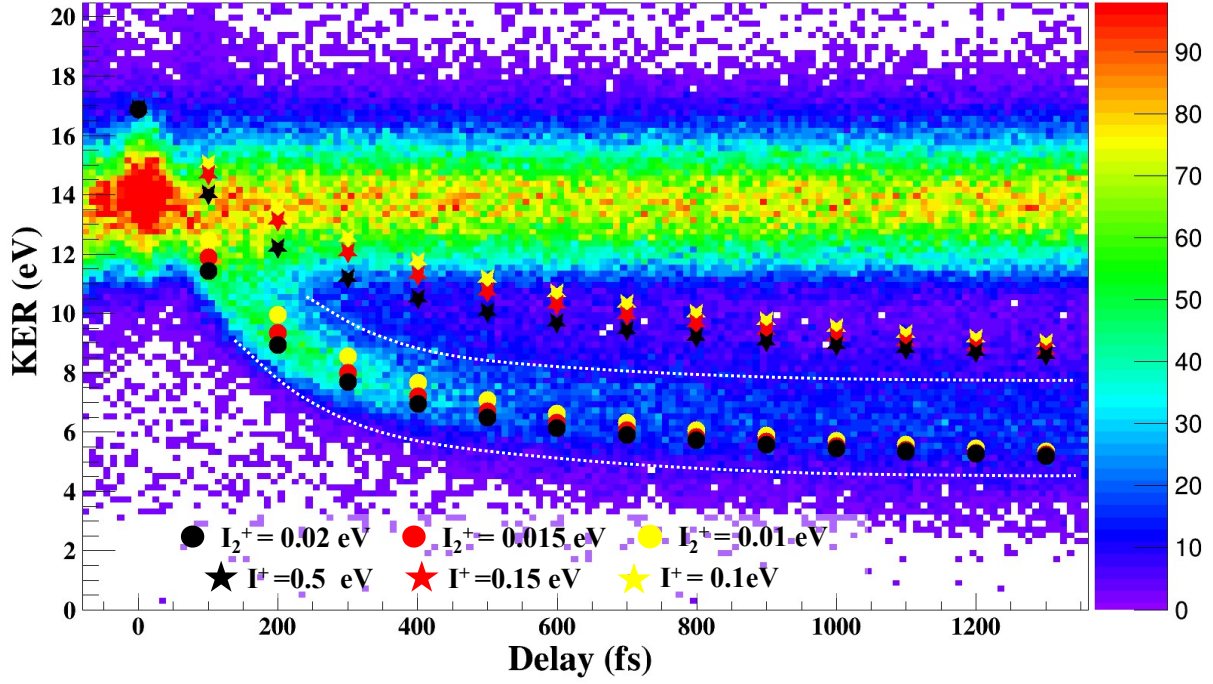


Figure 4.24: Delay-dependent KER distribution for the three-body $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ coincident channel. In this 2D plot, the KER of the coincident channel $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ is plotted as a function of delay between the pump and probe pulses. Colored symbols represent the simulated KER values at different delays assuming different asymptotic dissociation energies as indicated in the figure. Dashed lines indicate the descending delay-dependent KER feature. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

ionization channels (2) $\text{CH}_2\text{I}^+ + \text{I}$ and (3) $\text{CH}_2\text{I} + \text{I}^+$; I_2 elimination channels (4) $\text{CH}_2 + \text{I}_2^+$ and $\text{CH}_2^+ + \text{I}_2$, and, potentially, some three-body dissociation channels (although the latter have not been clearly identified so far). In addition, there should be some comparatively minor contribution from doubly charged pathways like $\text{CH}_2\text{I}^{2+} + \text{I}^+$ etc.

In Fig. 4.24, the measured KER for all $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ events is shown as a function of pump-probe delay. The overall structure of the graph is similar to two-body KER vs. delay spectra shown in Fig. 4.20, 4.22 and 4.23. First, there is a broad horizontal band between ~ 12 and 16 eV , reflecting CE of a bound molecule or a molecular ion. The KER of this band resembles the KER distribution measured for the same channel with a single NIR pulse (see Fig. 4.7). Second, a broad descending structure originating from CE of dissociating molecules can be also observed. However, the latter structure is less clear, and

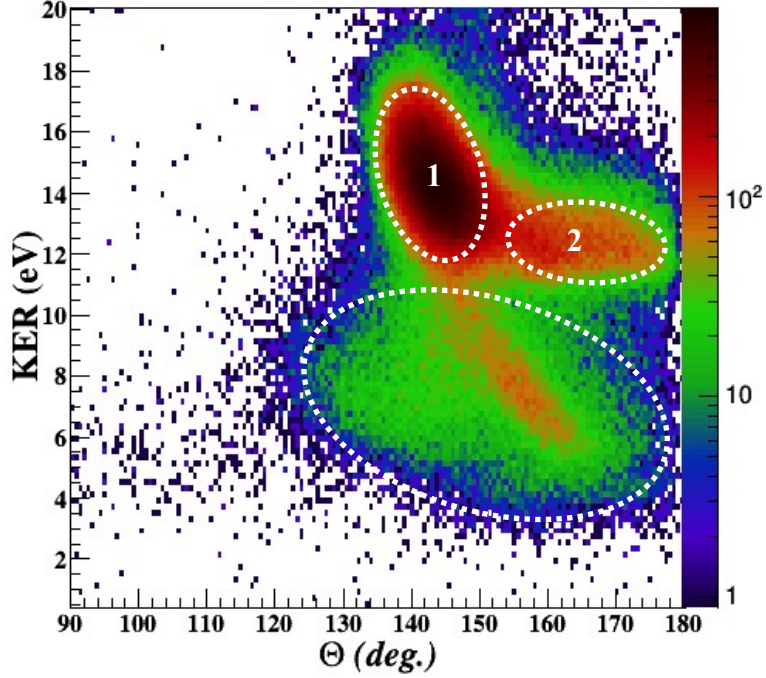


Figure 4.25: Delay-integrated KER- Θ plot for the three-body $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ coincident channel. This 2D plot is integrated over all delays from -100 fs to 1.4 ps. In the 2D plot, region (1) correspond to CE of bound molecule or fragments and the region (2) correspond to long-lived metastable CH_2I^{2+} ions, while the remaining events in the lower part of the graph reflect dissociating pathways.

there is also a significant number of events in-between the two bands. One reason for this is the addition of different “precursor” channels launched by the pump pulse. While in two-body breakup, for the fixed final-state channel, only one pair of fragments can form the dissociating precursor channel (like CH_2I and I for CE into CH_2I^+ and I^+). In contrast, for three-body analysis, either of two-body channels at lower charge states can contribute, causing significant broadening of the spectrum, as can be seen in the simulations for two different “precursor channels, $\text{CH}_2\text{I} + \text{I}$ and $\text{CH}_2 + \text{I}_2$, which are shown in this figure.

In Fig. 4.25 the same data are shown as a function of the KER and the angle Θ between the two measured iodine momentum vectors, integrated over the whole delay range shown in Fig. 4.24. Note that the events at the right border of this graph (180°) correspond to two iodine ions emitted back to back. This (KER, Θ) map can be subdivided into three areas, marked with dashed ovals in Fig. 4.25. Regions marked 1 and 2 correspond to a horizontal, delay-independent band in Fig. 4.24, and closely resembles the features present

in the corresponding single-pulse data shown in Fig. 4.7. As discussed in section 4.1, these regions mainly result from the concerted breakup of a bound molecule (region 1), or from sequential fragmentation of a long-lived metastable intermediate molecular ion like CH_2I^2+ (region 2). Since these are essentially single-pulse effects, the corresponding KER band in Fig. 4.24 is essentially delay-independent, beyond the region where the pump and the probe pulses overlap. The third area, with KER values below 12 eV, corresponds to broad descending structures in Fig. 4.24 and reflect the events where the molecule is fragmented by the pump.

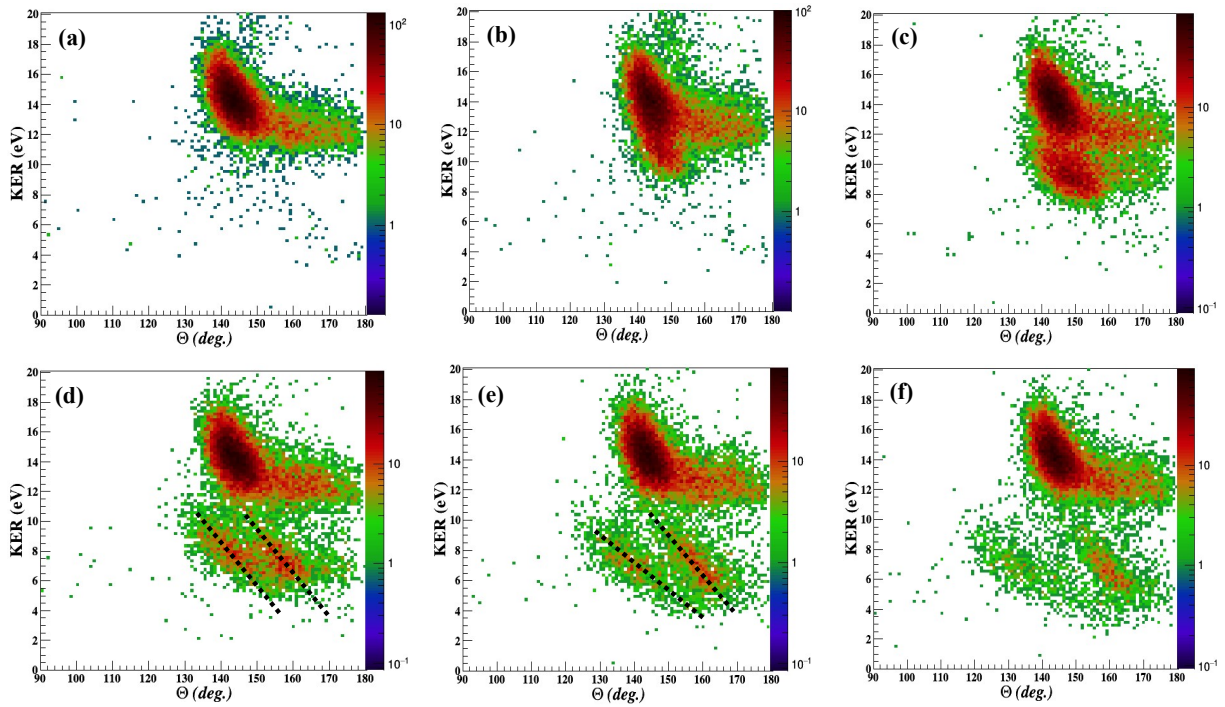


Figure 4.26: KER- Θ plots for the three-body $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ coincident channel at different delays: (a) $-50 \text{ fs} \rightleftharpoons 50 \text{ fs}$ (b) $50 \text{ fs} \rightleftharpoons 150 \text{ fs}$ (c) $150 \text{ fs} \rightleftharpoons 250 \text{ fs}$ (d) $400 \text{ fs} \rightleftharpoons 500 \text{ fs}$, (e) $700 \text{ fs} \rightleftharpoons 800 \text{ fs}$, and (f) $1.2 \text{ ps} \rightleftharpoons 1.3 \text{ ps}$. Dashed lines indicate two distinct low-KER features. Each snapshot is integrated over the corresponding 100 fs delay window.

In Fig. 4.26, such (KER, Θ) maps are shown at different pump-probe delays. The map at zero delay, where both pulses arrive at the same time (panel (a)) closely resembles the single-pulse data shown in Fig. 4.7, and consists mainly of the groups (1) and (2) marked in Fig. 4.25. Within next 50-150 fs, the main feature starts to evolve towards lower KERs (panel b), spreading also to larger angles at later times (panel c, 150-250 fs). At larger delays

(lower row), this feature, propagating towards lower KER values, splits into two rather broad, tilted structures marked by dashed lines in panels (d) and (e). To trace further evolution of these structures, we performed additional measurements at fixed delay values of 5 ps and 10 ps. The corresponding (KER, Θ) maps are shown in Fig. 4.27 (a) and (b), respectively. In these graphs, the right of the two structures at low KERs stays rather similar to the last panel of Fig. 4.26, whereas the left one spreads in angle and becomes rather flat (i.e., more “horizontal”), although only a few events seem to propagate towards energies below ~ 3 eV. At the same time, two groups of events at large KERs become more isolated from the descending features, and, at all delays, remain rather similar to single-pulse data.

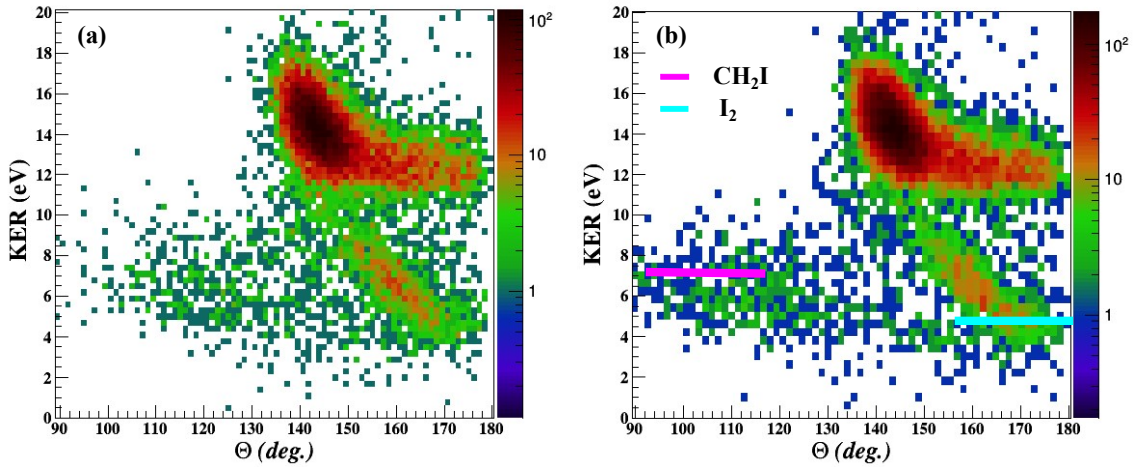


Figure 4.27: KER- Θ plots for the three-body $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ coincident channel at large delays: (a) 5 ps, and (b) 10 ps. Solid colored lines represent the simulated KER values for the two-body CE of the intermediate reaction product after the removal of the second electron (pink for CH_2I and cyan for I_2 fragments).

To understand the delay-dependent evolution of the three-body CE explosion patterns shown in Fig. 4.25 - 4.27, we need to consider all potentially relevant dissociation channels. Here, we effectively treat the CH_2I_2 molecule as triatomic, with CH_2 group always remaining bound. This is justified since by fixing the final state in our coincident measurement to $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$, we reliably exclude all the events where one or both hydrogens are detached. Correspondingly, in terms of nuclear motion there are only three distinct possibilities for dissociation by the pump pulse, leading to $\text{CH}_2\text{I} + \text{I}$, $\text{CH}_2 + \text{I}_2$ and $\text{CH}_2 + \text{I} + \text{I}$ channels, where each of the fragments might be either neutral or singly charged. These three channels are

expected to have distinctly different contributions to the three-body CE patterns considered here. For both two-body channels, the initial expectation of how their contribution should look like can be obtained from the CE simulations discussed in section 2.5 (and plotted for the same (KER, Θ) map for higher final charge state in Fig. 2.20). As can be seen from Fig. 2.20 (a), the channel resulting in I_2 formation and elimination is expected to converge to back-to-back emission of both iodines at large delays, since the influence of the CH_2^+ Coulomb repulsion becomes negligible. In contrast, the channel including the detachment of one iodine and CH_2I (see Fig. 2.20 (b)) can have a much broader angular distribution, strongly dependent on the details of CH_2I rotation. In terms of KER, both of these channels at large delays should converge to a certain non-zero limit, given by the CE of the fragment that remains bound after the pump (i.e., CH_2I / CH_2I^+ or I_2 / I_2^+). The expected limits for the CE obtained from the CE simulation are shown as horizontal magenta (CH_2I) or cyan (I_2) lines in Fig. 4.27 (b). We should remember here though that such a CE simulation always tends to overestimate CE energy for bound molecules. The third dissociation pathway, the three-body dissociation, doesn't have such a clear limit, and is expected to propagate to even smaller KERs, finally approaching the limit given by the translational energy of the dissociation process itself.

Disentangling molecular iodine elimination and other dissociation channels

To reliably identify signatures of different dissociation channels discussed above, and to discriminate between them, we now consider the sum kinetic energies (KE) of two iodine fragments only, which is expected to behave very differently for the major two-body dissociation pathways. For the $CH_2I + I$ channel, the detached iodine should have the KE decreasing as a function of the delay due to decreasing Coulomb repulsion, which becomes very low at large delays. The second iodine is always close to CH_2 , and, because of its larger mass, takes a small fraction of its CE energy after the CE of CH_2I (or CH_2I^+) by the probe. Therefore, for this channel, the sum KE of two iodines should decrease with the delay towards rather low values. In contrast, for the I_2 formation, at large delays the influence of the

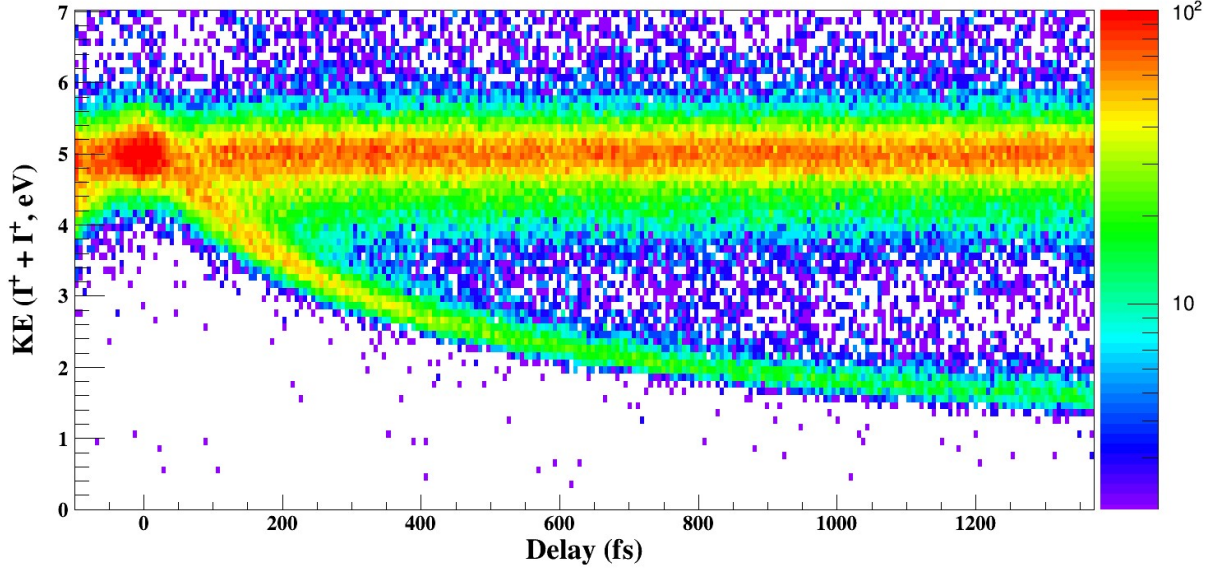


Figure 4.28: Delay-dependent sum KE distribution of the two I^+ fragments from the $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ coincident channel. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

CH_2^+ fragments become negligible, and the sum KE of the two iodines is then given by the CE of the bound I_2 (or I_2^+), as shown by the cyan line in Fig. 4.27 (b). So in this case, we expect the sum KE of both iodine fragments to converge towards 4-5 eV, and exhibit little delay dependence. This intuitive view is consistent with the predictions of CE simulations.

The measured delay-dependent sum KE energies of two iodine fragments is shown in Fig. 4.28. It exhibits a clear, sharp descending line and a strong horizontal band centered at ~ 5 eV. Since the latter band is dominated by the CE of bound molecules, in order to focus on dissociative channels, in Fig. 4.28 we plot the same graph for the values of the total KER above (a) and below (b) 12 eV. As can be seen in Fig. 4.24-4.27, for the delays beyond 150-200 fs, the $\text{KER} < 12 \text{ eV}$ corresponds to the features descending in total KER, which reflect the dissociation on the molecules. The corresponding sum KE spectrum of the two iodines again displays two bands, one descending towards 1 eV at large delays, and another one, between 4 and 5 eV, which remains nearly constant even for this low-KER selection. We assign this upper band to the formation of molecular iodine (I_2 or I_2^+), whereas the descending band is likely dominated by the $\text{CH}_2\text{I} + \text{I}$ channel, where one of the partners is likely singly charged. This assignment is in perfect agreement with the predictions of the

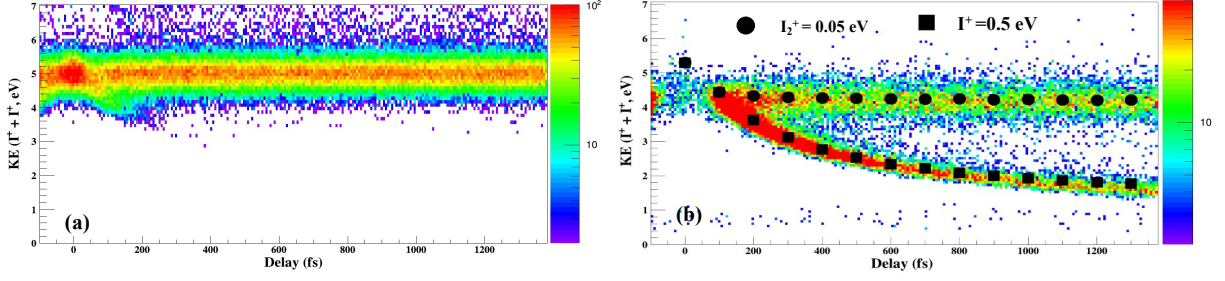


Figure 4.29: Delay-dependent sum KE distribution of the two I^+ fragments from the $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ coincident channel for different total KER conditions. (a): $\text{KER} > 12$ eV. (b): $\text{KER} < 12$ eV. Black symbols in (b) represent the simulated values at different delays assuming that the pump pulse triggers $\text{CH}_2 + \text{I}_2^+$ (circles) or $\text{CH}_2\text{I} + \text{I}^+$ (squares) dissociation channel. The asymptotic energies of the fragments are indicated in the figure. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14}$ W/cm² while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14}$ W/cm².

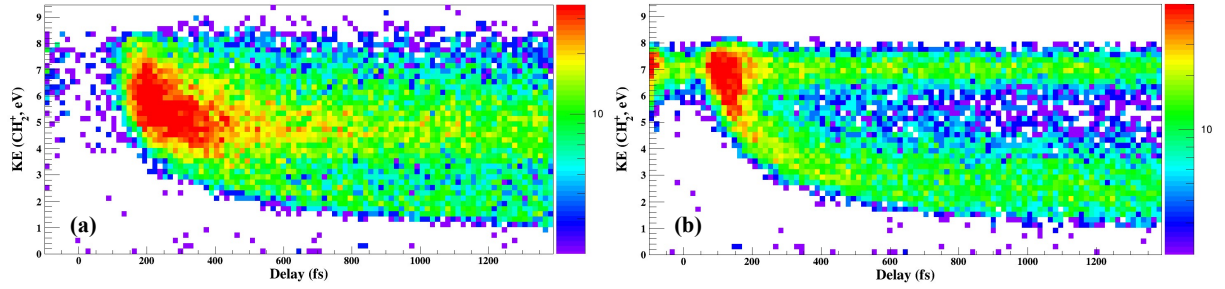


Figure 4.30: Delay-dependent sum KE distribution of CH_2^+ fragments in the three-body coincident channel for KER below 12 eV. Panel (a) corresponds to events with the sum KE ($\text{I}^+ + \text{I}^+$) in the range 0 - 3.80 eV. Panel (b) contains the events with the sum KE ($\text{I}^+ + \text{I}^+$) in the range 3.80 - 6.0 eV.

corresponding CE simulations also shown in Fig. 4.29 (b). To further elaborate on this, in Fig. 4.30, we plot the CH_2^+ energies as a function of the delay for the conditions of Fig. 4.29 (b) (i.e., total KER < 12 eV), but separated according to the sum KE of two iodines. In Fig. 4.30 (a), for the iodine sum KE < 3.8 eV, the CH_2^+ KE distribution is dominated by a rather broad band converging to 3-6 eV at large delays, with a weaker and narrower feature at lower KE. In contrast, the CH_2^+ KE for large iodine sum KE (3.8 – 6 eV) in Fig. 4.30 (b) is dominated by a more distinct descending band converging towards 1-3 eV at large delays, which is consistent with the assumption that this results from $\text{CH}_2 + \text{I}_2$ precursor channel. A weaker horizontal band at ~ 7 eV is most likely an indication of some contribution from high-KER regions (1) and (2) of Fig. 4.25, which are not completely filtered out by the

condition $\text{KER} < 12$ eV.

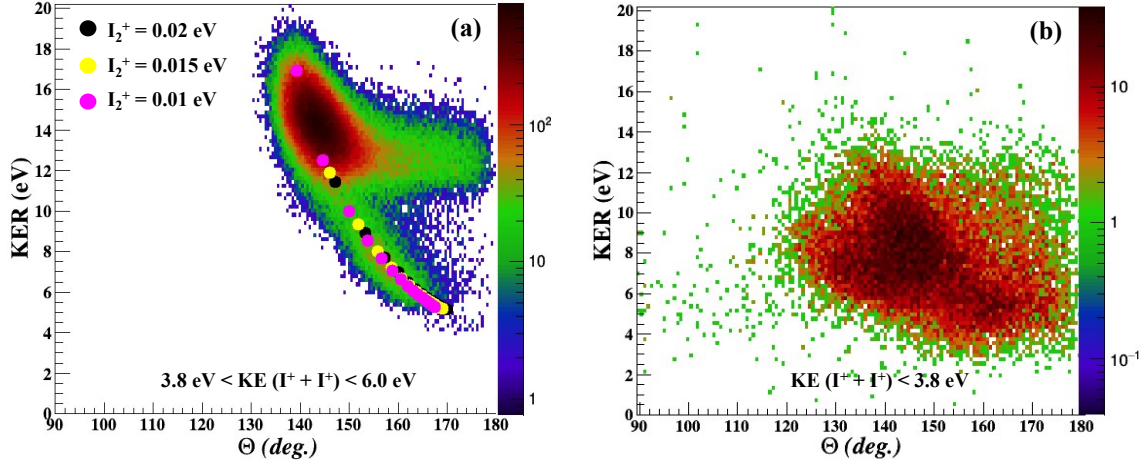


Figure 4.31: KER- Θ plots for the three-body coincident $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ channel for different sum KE ($\text{I}^+ + \text{I}^+$) conditions. The data are integrated over the whole delay range (from -100 fs to 1.4 ps). In panel (a), the sum KE ($\text{I}^+ + \text{I}^+$) is set to be within the range of 3.80 - 6.0 eV. In panel (b), the sum KE ($\text{I}^+ + \text{I}^+$) < 3.80 eV condition is applied. Solid circles represent the simulated values at different delays assuming $\text{CH}_2 + \text{I}_2^+$ dissociation after the pump pulse with the I_2^+ translational energies as indicated by symbols.

In Fig. 4.31 we plot the delay-integrated (KER, Θ) maps with the condition that the sum (I, I) KE is large (between 3.8 - 6 eV, panel (a)) or small (< 3.8 eV, panel (b)). Since this map explicitly shows the KER value, we do not employ any additional conditions on KER. Panel (a) thus contains either the events from the CE of bound molecule or sequential channels at large KERs, and a descending band resulting from I_2^+ or I_2 elimination. As expected, this band converges towards large angles. The results of CE simulation for this channel shown in Fig. 4.31 (a) are in a good agreement with the experiment. Fig. 4.31 (b) contains the events resulting from other dissociation channels, which we will discuss in more detail later, using delay-dependent plots. It should be noted that the onset region for those channels (at high KERs) is artificially cut out from this plot (and are, in fact, included in panel (a)) because, as can be seen from Fig. 4.29 - 4.30, for small delay below 150-200 fs, the sum iodine KE on the descending band is still above 3.8 eV.

Figure 4.32 displays the (KER, Θ) maps with the same two conditions as in Fig. 4.31, but measured at the delays of 5 ps (a,b) and 10 ps (c,d). In panels (a) and (c) on the left, which focuses on molecular iodine elimination, the corresponding feature (marked 3

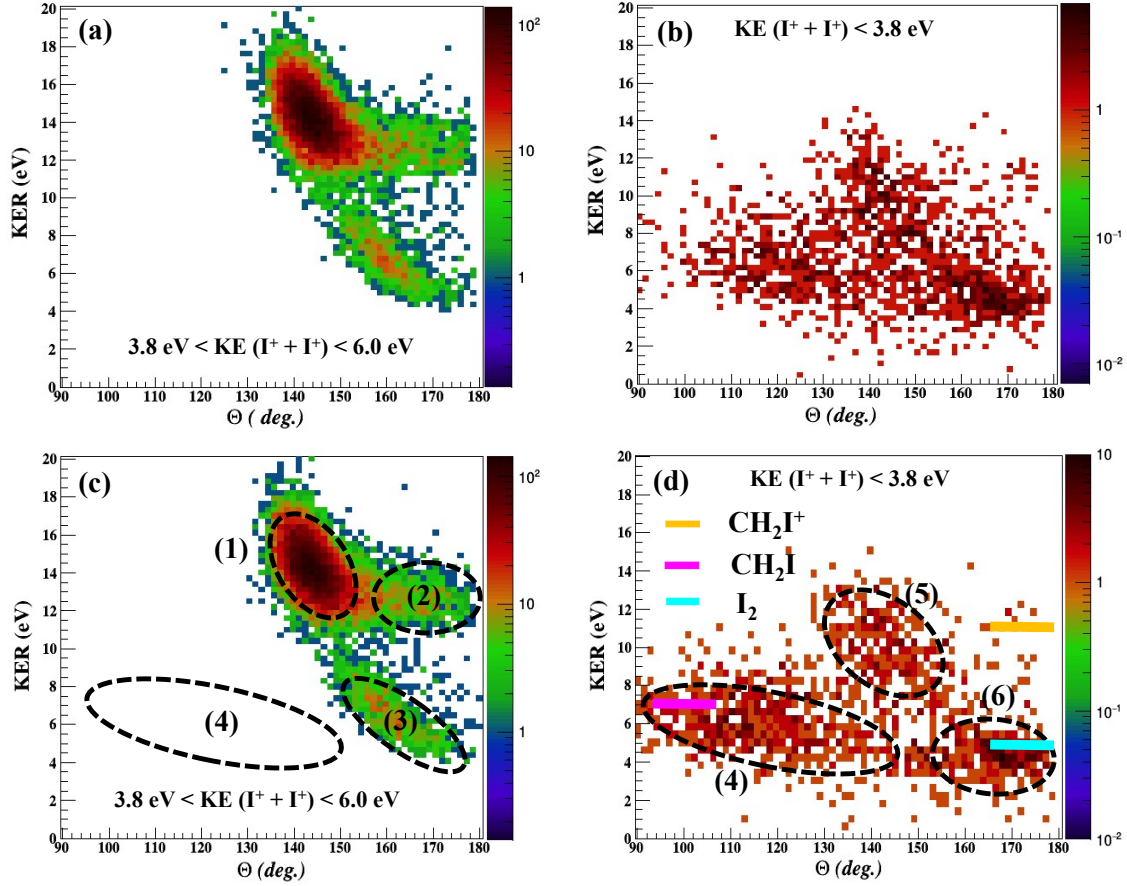


Figure 4.32: KER- Θ plots for the three-body coincident $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ channel for different sum KE ($\text{I}^+ + \text{I}^+$) conditions at large delays. Here, panels (a) and (b) correspond to the KER- Θ plots at 5 ps, where panels (c) and (d) correspond to the KER- Θ plots. Solid pink and cyan lines in panel (d) represent the simulated asymptotic CE energies at infinitely large delay for $\text{CH}_2\text{I} + \text{I}$ or $\text{CH}_2 + \text{I}_2$ dissociation channels, respectively (neglecting the translational dissociation energies) (the same as the values shown in Fig. 4.27 (b)). The yellow solid line represents the simulated KER value for the channel $\text{CH}_2\text{I}^+ + \text{I}^+$ initiated by the pump pulse.

in (c)) becomes well-separated from the delay-independent high energy bands, approaching 180 degree angle between the momenta of two iodines and staying nearly the same for both delays. In panels (b) and (d), with the condition on low iodine sum KE, the distribution still evolves considerably between 5 ps (b) and 10 ps (d), with three distinct structures (marked 4, 5 and 6) formed at 10 ps. While structure (4) is completely eliminated in the left panels of Fig. 4.32, for the other two features there is a noticeable amount of events in these areas.

To further elaborate the assignment of different structures observed in our three-body

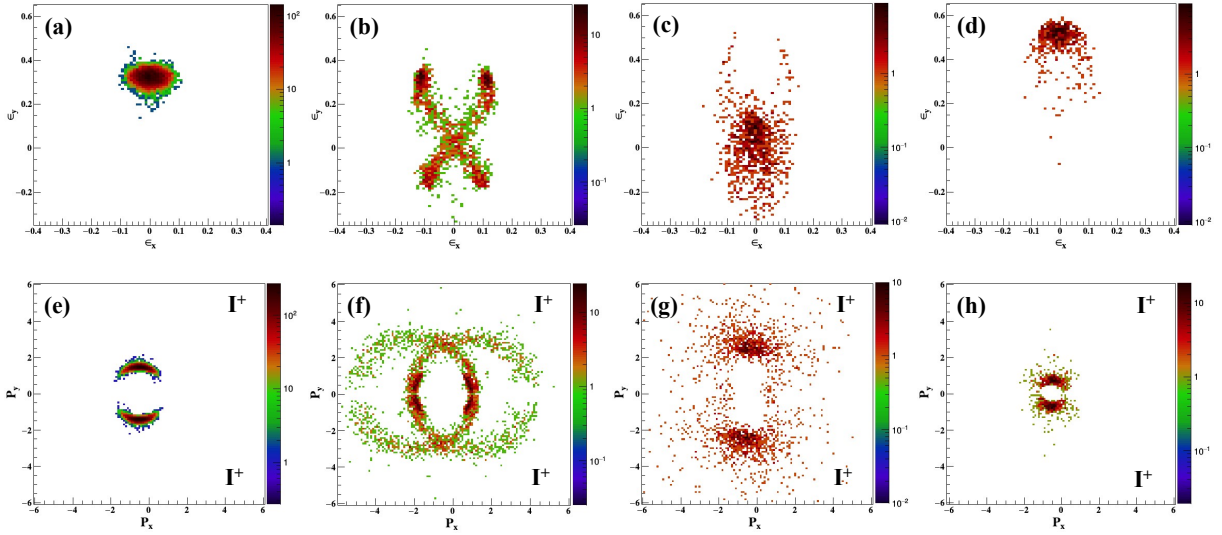


Figure 4.33: Dalitz and Newton plots for the different regions of KER- Θ plot of three-body coincident $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ channel at 10 ps. Here, panels (a-d) in upper row are the Dalitz plots for the corresponding KER- Θ regions numbered as (1) to (4) in Fig. 4.32. Panels (e-h) in the lower row are the Newton plots for the corresponding KER- Θ regions numbered as (1) to (4) in Fig. 4.32.

CE patterns, in Fig. 4.33, we analyze Dalitz plots (top row) and Newton diagrams (bottom row) of the data from regions 1-4 at 10 ps, which can be clearly separated from each other. As explained in section 2.5, (see also Fig. 2.16), these representations of three-body fragmentation provide additional intuitive insight into energy sharing and momentum correlations of the fragments, respectively. As can be seen from panels (a, e), and (b, f) for regions (1) and (2), respectively, these regions display the patterns identical to those obtaining with a single pulse (see Fig. 4.8 - 4.9) that are characteristic for the concerted breakup of a bound molecule (region 1, panels a, e), and for the sequential fragmentation of long-lived metastable states (region 2, panels b, d), as detailed in section 4.1. The patterns for regions 3 and 4 look very different. For region 3 (panels c, g), the fraction of energy taken the CH_2^+ fragment is rather small, such that the corresponding events fall into lower part of the Dalitz plot in Fig. 4.33 (c), and iodine momenta scaled to that of the CH_2^+ are large and directed mostly back to back (see Fig. 4.5 (g)). This confirms our assignment of this channel to I_2 elimination. In contrast, for region 4 (panels d, f), which we assign to CH_2I or CH_2I^+ formation, the fraction of CH_2^+ energy is very large (Fig. 4.34 (d)), while the relative iodine momenta are

low (Fig. 4.33 (h)). They also span a broad range of relative emission angles, most likely, due to rotation of the intermediate CH_2I fragment.

Besides these clear assignments, there are two structures marked 5 and 6 in Fig. 4.32 (d) that overlap with features 1-3 in (KER, Θ) maps. Based on the combination of its rather high KER and low iodine sum KE, we assign structure 5 to the pathway, where the pump pulse initiates the CE of the molecule ($\text{CH}_2\text{I}^+ + \text{I}^+$). According to our CE simulation, its KER of ~ 11 eV at large delays consists mostly of the CE energy from the pump step (~ 4 eV), and then of the energy release in the CE of the CH_2I^+ ion by the probe (~ 7 eV). While the iodine KE for this pathway are rather low (~ 2 eV for the first step and ~ 0.7 eV for the second), and their sum mostly falls below 3.8 eV, the high-energy tail of channel might also provide some background contribution to our selection of I_2 elimination events. Channel 6 is somewhat more complicated to assign. In general, it exhibits most of the features typical for I_2 elimination (in particular, preferential back to back emission of two iodines), but has both, its KER and iodine sum KE slowly drifting towards very small values with the increasing delay, even in 5 to 10 ps region. Our current hypothesis for this channel assumes that these events result from the creation of metastable I_2^{x+} fragment, where x can range from 0 to 2, which decays on a ps time scale comparable with our delay range. If the probe pulse arrives before this decay, the event falls into the I_2 elimination range of observables. If, however, it decays before the probe pulse, than we are sampling two iodines at slowly increasing internuclear separations, resulting in decreasing KE. Finally, a small number of scattered events propagating towards zero KER most likely originates from three-body dissociation after the pump pulse, since at large delays they experience only very small Coulomb repulsion.

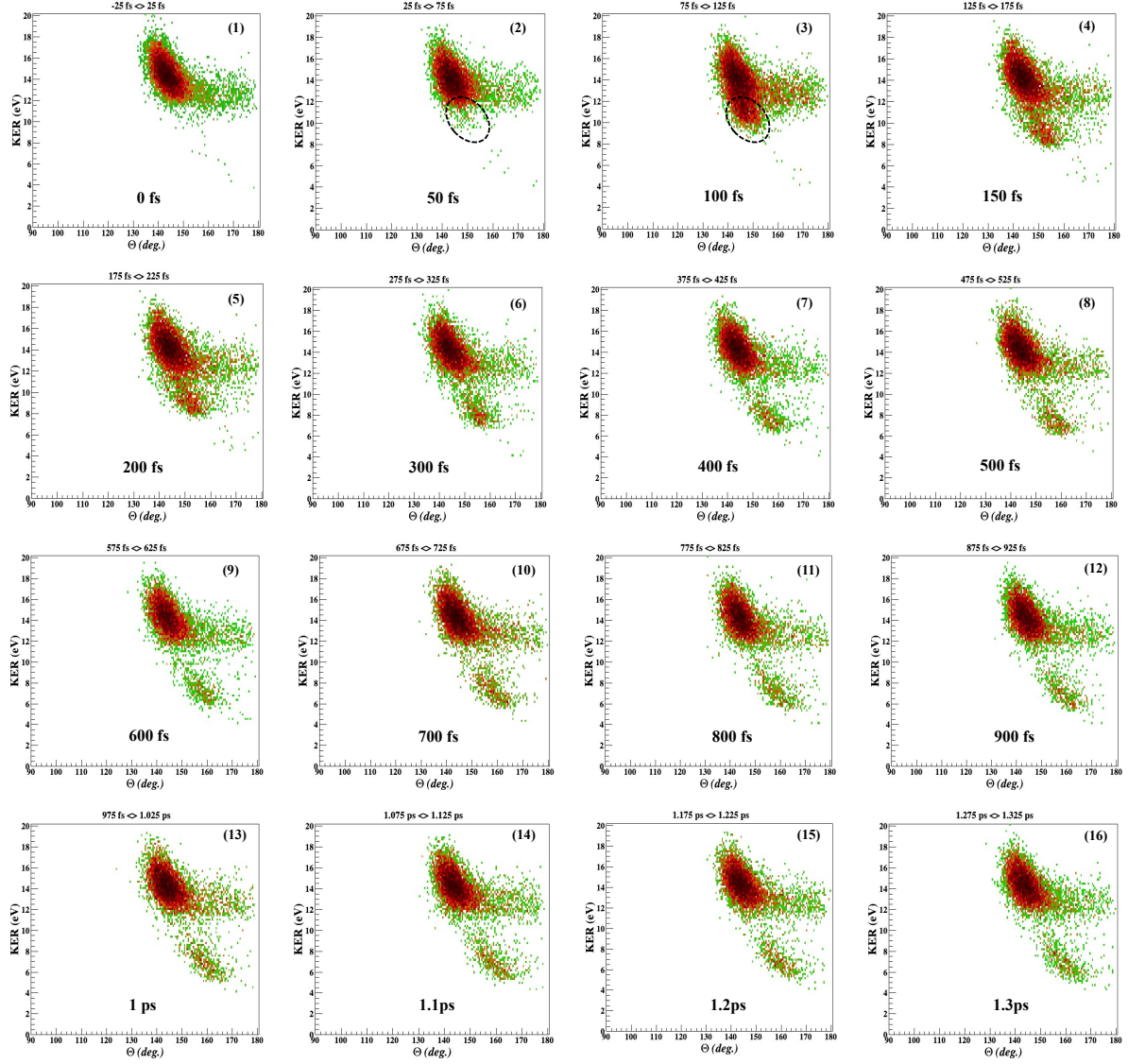


Figure 4.34: KER- Θ plots for the three-body coincident $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ channel involving I_2 formation channel (selected by the condition that the sum KE of the two I^+ fragments lie between 3.6 and 6 eV). There are 16 snapshots numbered from (1) to (16), and each snapshot corresponds to the 50 fs delay window centered at the values shown in the figure.

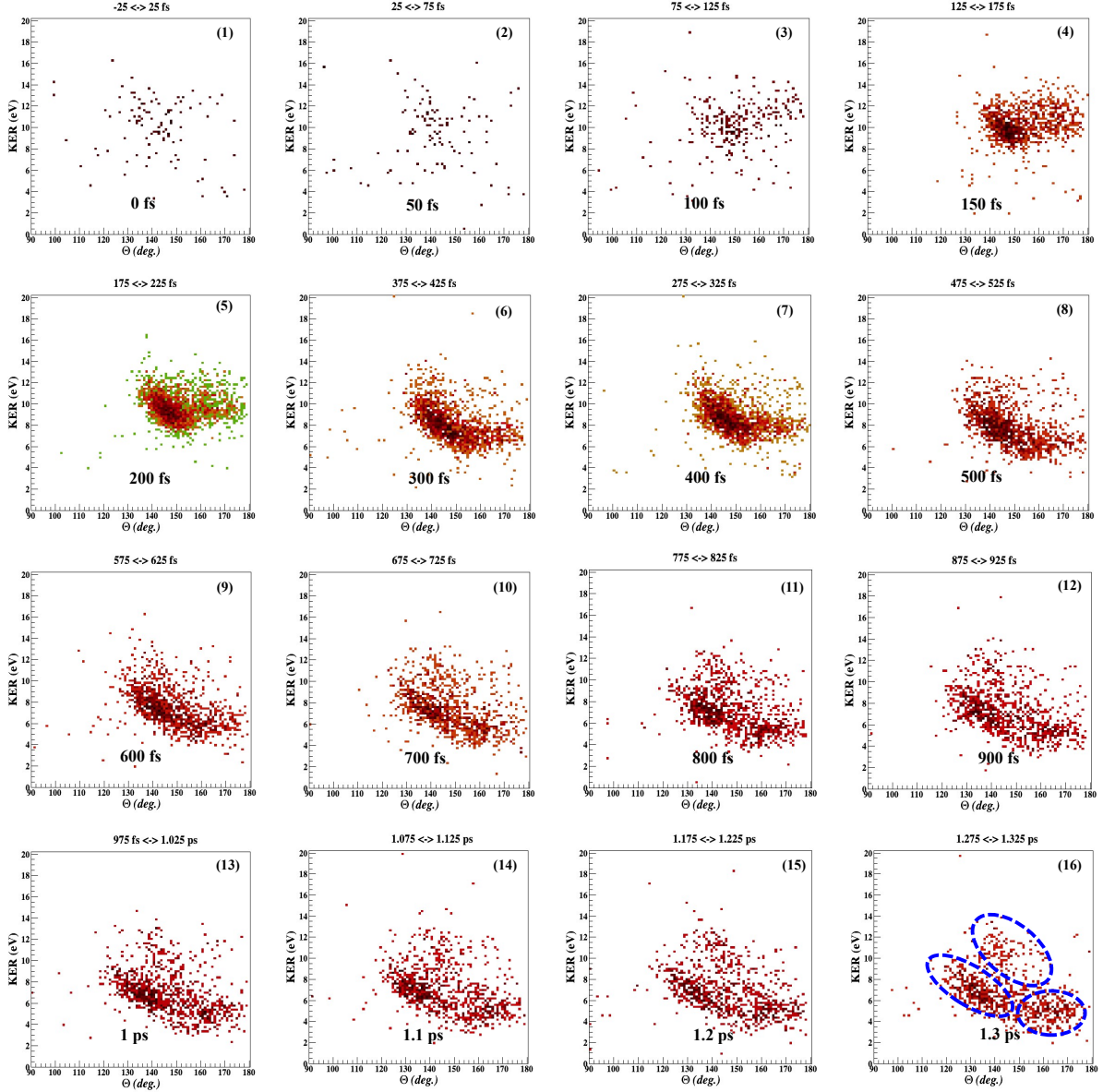


Figure 4.35: KER- Θ plots for the three-body coincident $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$ channel under the condition that the sum KE of the two I^+ fragments is below 3.6 eV. There are 16 snapshots numbered from (1) to (16), and each snapshot corresponds to the 50 fs delay window centered at the values shown in the figure.

With all these assignments in mind, we now can create “a movie” visualizing molecular iodine elimination pathway. It is shown in Fig. 4.34 in frames of 50 fs, clearly highlighting the time evolution of the I_2 ejection and propagation. From these movie and from the above comparison with the CE simulation it is rather clear that our observations are consistent only with direct, “synchronous” I_2 elimination. A complementary view of the other channels,

selected with the condition on (I,I) sum KE below 3.8 eV, is presented in Fig. 4.35. There, one can trace the time evolution of structures 4-6 discussed above in relation to Fig. 4.32 (marked with blue dashed ovals in the last frame of the presented series of snapshots).

4.4 Strong-field induced dynamics in CH₂ICl

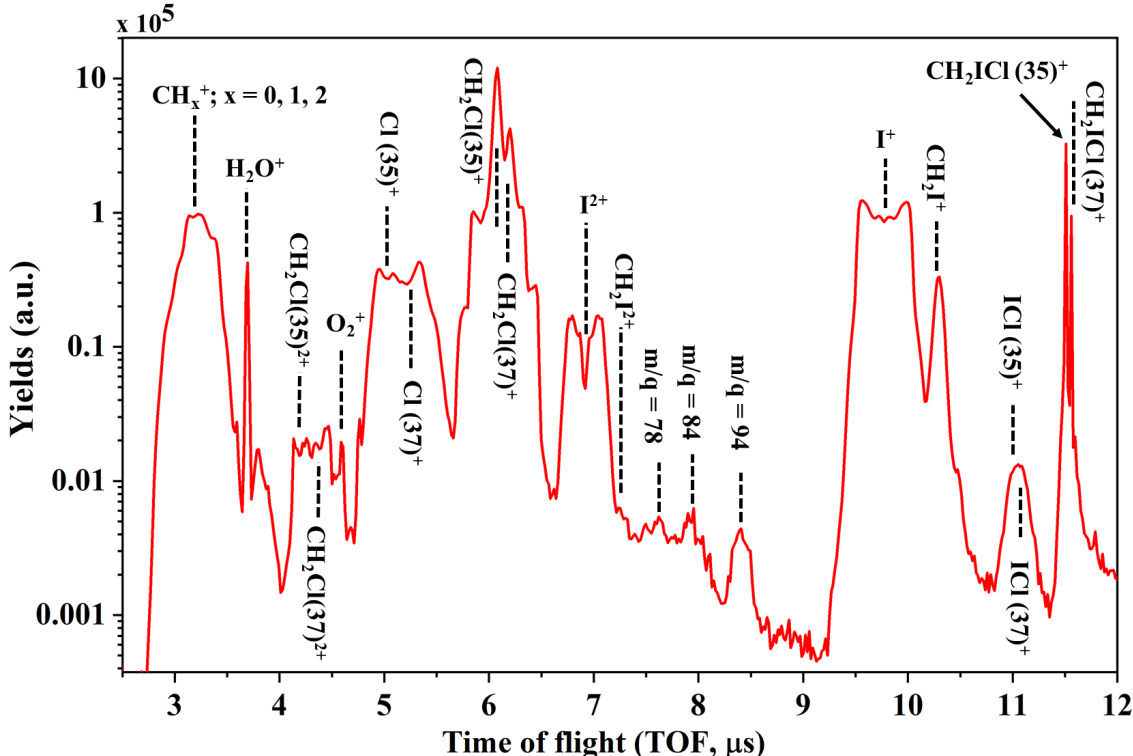


Figure 4.36: Time of flight (TOF) plot of ions of CH₂ICl molecule after a single NIR pulse. In this plot, TOF values of ions resulting from CH₂ICl fragmentation in presence of strong-field are labeled based on their mass-to-charge ratio. Intensity of the laser pulse is kept at $\sim 2 \times 10^{14}$ W/cm².

In order to verify which of the findings and observations described in the previous sections can be generalized for other polyatomic systems and, in particular, to other dihalomethanes, we have carried out a similar set of experiments on chloridomethane molecules (CH₂ICl). Besides the lighter mass of the molecule and the presence of two Cl isotopes, the major difference for our type of experimental analysis compared to CH₂I₂ case is the distinguishability of the two halogen atoms. This changes visual appearance of all three-particle maps, in general

making them asymmetric, and enables a larger variety of dissociation pathways, associated with the detachment of different halogen atoms. Below, we present a brief overview of the main results of CH_2ICl experiments. The experimental conditions were set identical to one of the settings of the CH_2I_2 experiments, with the intensities of pump and probe pulses (800 nm, 25 fs) set to $2 \times 10^{14} \text{ W/cm}^2$ and $4 \times 10^{14} \text{ W/cm}^2$, respectively.

CH_2ICl molecule under a single NIR pulse

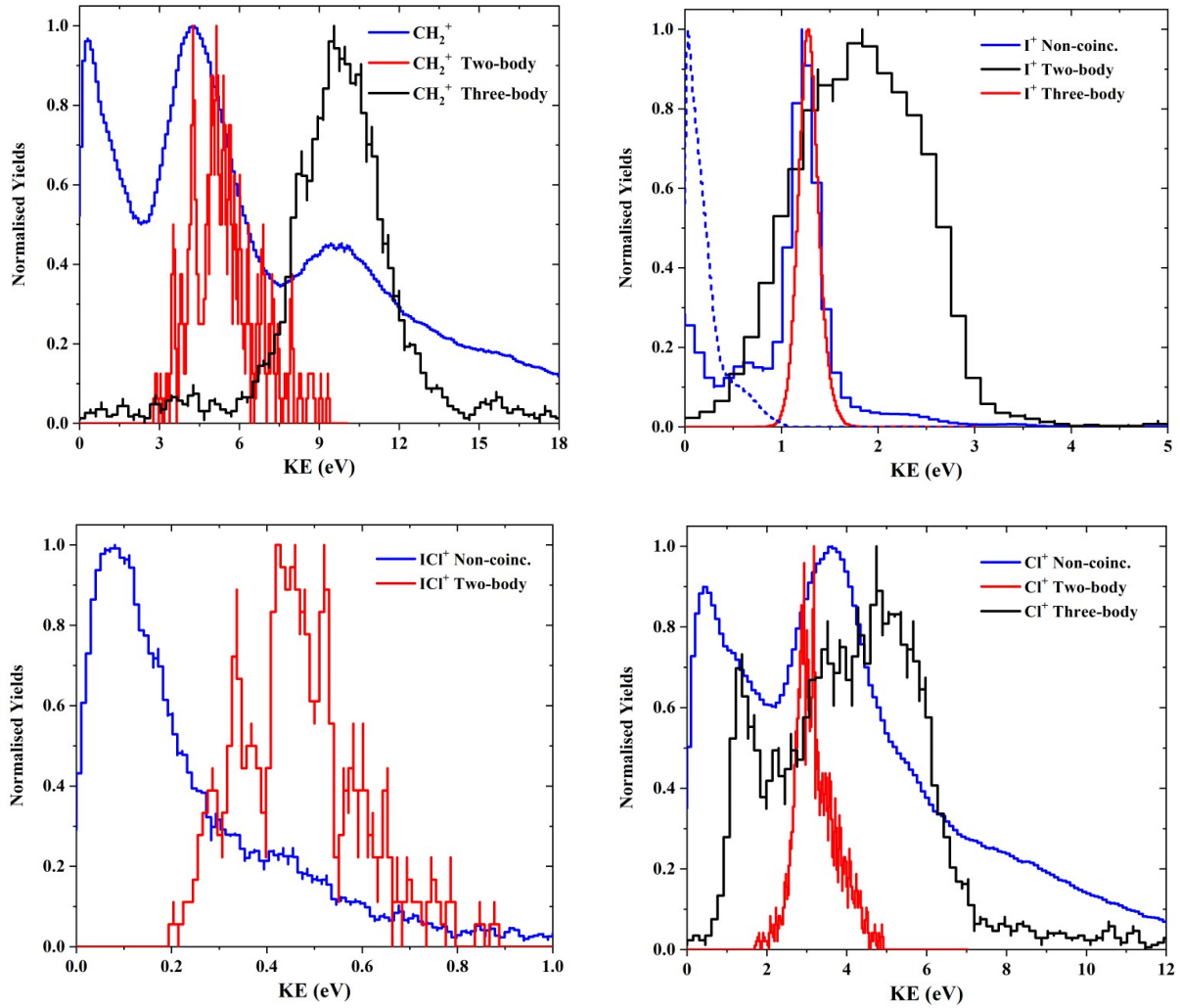


Figure 4.37: Kinetic energy (KE) distributions of fragments of CH_2ICl molecule after a single NIR pulse. In this 1D plot, the KE distributions of CH_2^+ , I^+ , ICl^+ and Cl^+ fragments are plotted and are indicated by the blue color. The KE distributions in red and black color represent the corresponding fragments in two- and three- body coincident channels, respectively. Intensity of the laser pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$.

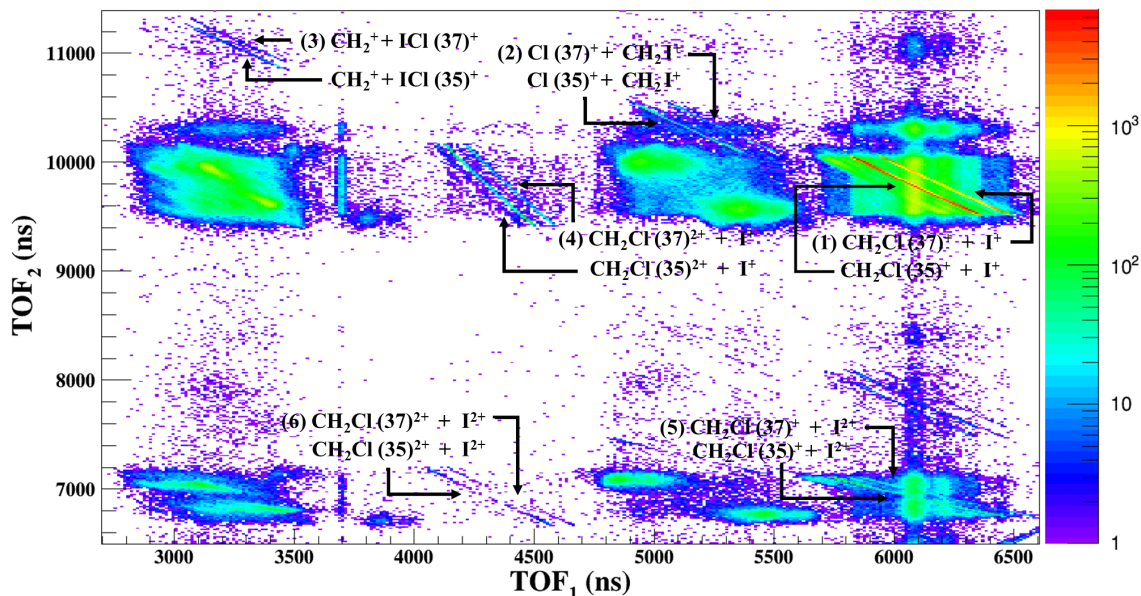


Figure 4.38: Photoion-photoion coincidence (PiPiCo) plot for the fragmentation of CH_2ICl molecule after a single pulse. In this 2D plot, the time of flight (TOF_1) of a lighter fragment is plotted against the time of flight (TOF_2) of a heavier fragment. The coincident channels are identified as the diagonal lines and are labeled based on their TOF values. Intensity of the laser pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$.

Like in the CH_2I_2 molecule, the laser irradiation on the CH_2ICl molecular target results in many possible ionization and fragmentation channels. The ion fragments detected after such interaction are presented in the non-coincident ion TOF spectrum shown in Fig. 4.36, and in coincident two-particle and three-particle TOF patterns (“PiPiCo spectra”) shown in Fig. 4.38 and Fig. 4.39, respectively. The deduced KE energies of the major products (non-coincident and coincident) are depicted in Fig. 4.37. The major TOF peaks and their structure is rather similar to those discussed for CH_2I_2 in Fig. 4.1, with the addition of the CH_2ICl^+ and Cl^+ fragments, and the doubling of the parent ion peak because of the existence of ^{35}Cl and ^{37}Cl isotopes with comparable natural abundance. While these are also present in all other chlorine-containing fragments, their appearance is buried under broad momentum distributions reflected in the corresponding TOF peaks in Fig. 4.36. The contribution of individual isotopes in coincident spectra can be readily identified as separate lines in two- and three-body PiPiCo spectra in Fig. 4.38 and 4.39. In the following analysis of KE and momenta, we focus on the channels containing ^{35}Cl isotope.

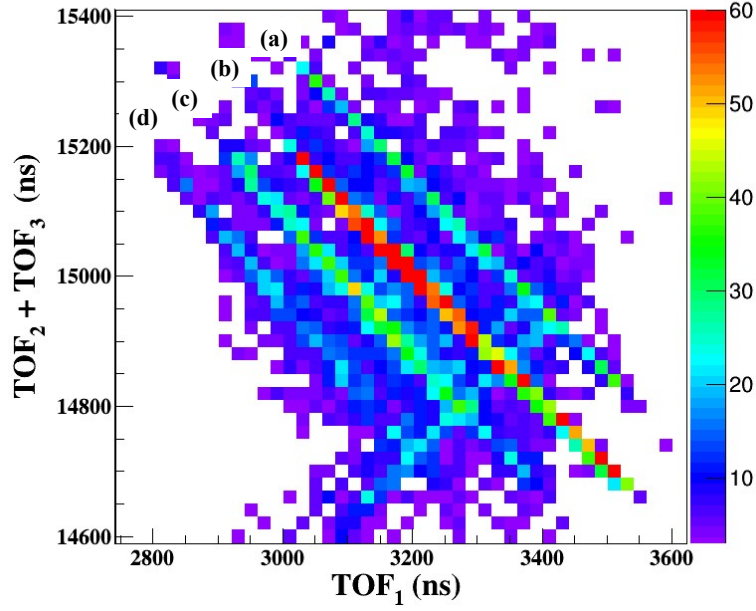


Figure 4.39: Three-particle photoioncoincidence (“TriPiCo”) plot for the three-body breakup $\text{CH}_2^+ + \text{Cl}^+ + \text{I}^+$ channel after a single NIR pulse. In this 2D plot, the time of flight (TOF_1) of CH_x^+ ($x = 0, 1$ and 2) is plotted against the sum of time of flight of Cl^+ (TOF_2) and I^+ (TOF_3) fragments. The three-body breakup coincident channels (a), (b), (c) and (d) are labeled based on their TOF information. The channel labeled as (a) is $\text{CH}_2^+ + \text{Cl}(37)^+ + \text{I}^+$ and the channel labeled as (b) is mainly $\text{CH}_2^+ + \text{Cl}(35)^+ + \text{I}^+$. Channels (c) and (d) contain $\text{Cl}(35)^+$ and I^+ fragments with the CH^+ and C^+ fragments, respectively. Intensity of the single pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$.

Fig. 4.40 displays the (KER, Θ) map obtained using a single NIR pulse for $\text{CH}_2^+ + {}^{35}\text{Cl}^+ + \text{I}^+$ final state, along with the 1D KER spectrum and the KE distribution of three individual fragments. Here, Θ is the angle between the measured momentum vectors of Cl^+ and I^+ ions. The (KER, Θ) plot contains the same two features as the analogous CH_2I_2 pattern shown in Fig. 4.7: (1) a tilted oval at $\sim 16 \text{ eV}$ and slightly below 140° , and a horizontal structure at slightly lower KERs extending to 180° . Here again, these two structures reflect concerted breakup of a bound molecule and the sequential fragmentation of long-lived metastable intermediate dications, respectively [72]. Characteristic signatures of both of these channels can be readily identifies in Dalitz and Newton plots shown in Fig. 4.41. In the Dalitz plot (panel a), the events from the concerted breakup appear as the intense tilted band shifted to the right, while the longer and the shorter diagonal features reflect the long-lived metastable $\text{CH}_2\text{Cl}^{2+}$ and CH_2I^{2+} intermediates. These channels appear

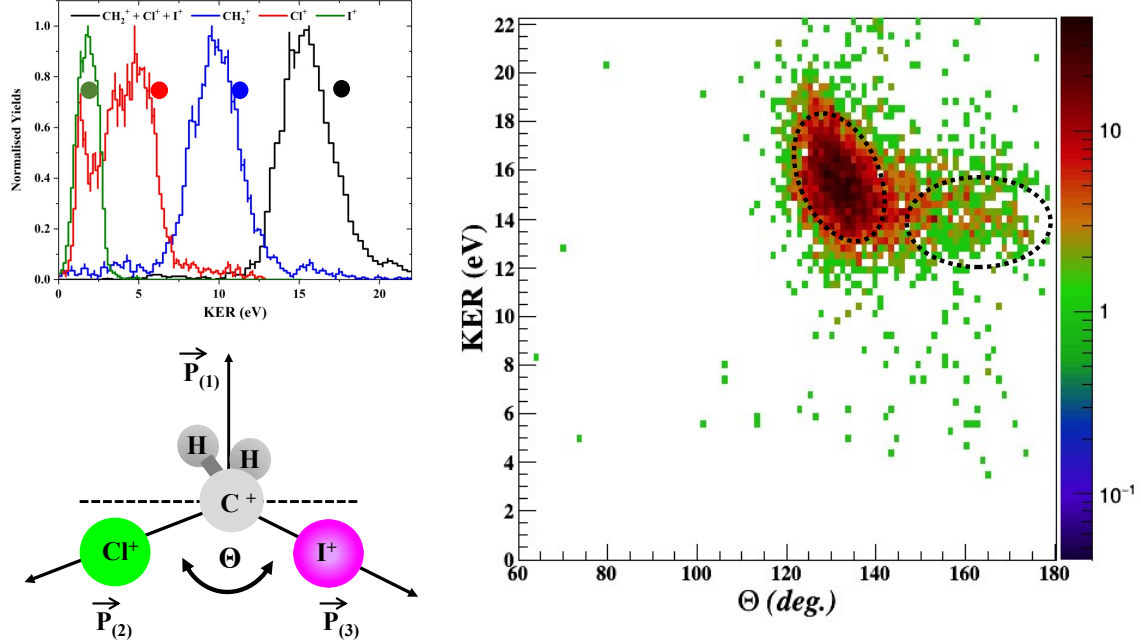


Figure 4.40: KER- Θ plot for the 3-body coincident $\text{CH}_2^+ + \text{Cl}(35)^+ + \text{I}^+$ channel after a single pulse. In this 2D map, the yield of the three-body events are plotted for different KER values and emission angles. The 1D KER distribution along with the definition of emission angle “ Θ ” is shown on the left of 2D map. The yields of the fragments in the 1D plot are normalised to 1 with respect to maximum yield. Intensity of the laser pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$.

as sprinkle-like features marked (1) and (2) in the Newton diagram shown in Fig. 4.41 (b).

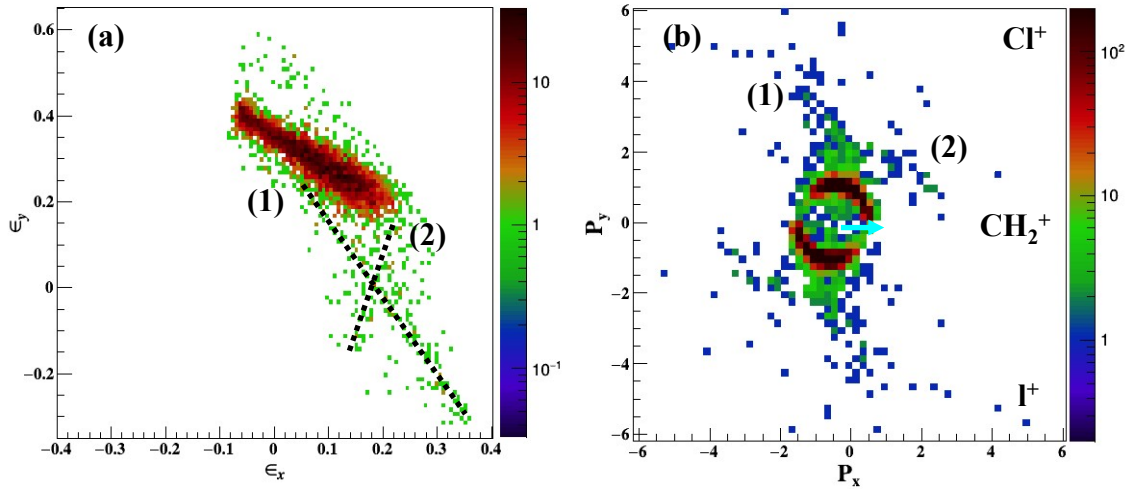


Figure 4.41: Three-body plots for the coincident $\text{CH}_2^+ + \text{Cl}(35)^+ + \text{I}^+$ channel in $\text{CH}_2\text{Cl}^{2+}$ after a single pulse. (a) Dalitz plot, (b) Newton diagram. Dashed lines mark the distinct features in Dalitz plot corresponding to the production of metastable intermediates. Intensity of the laser pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$.

Mapping different dissociation pathways and ICl^+ elimination via two-body fragmentation channels

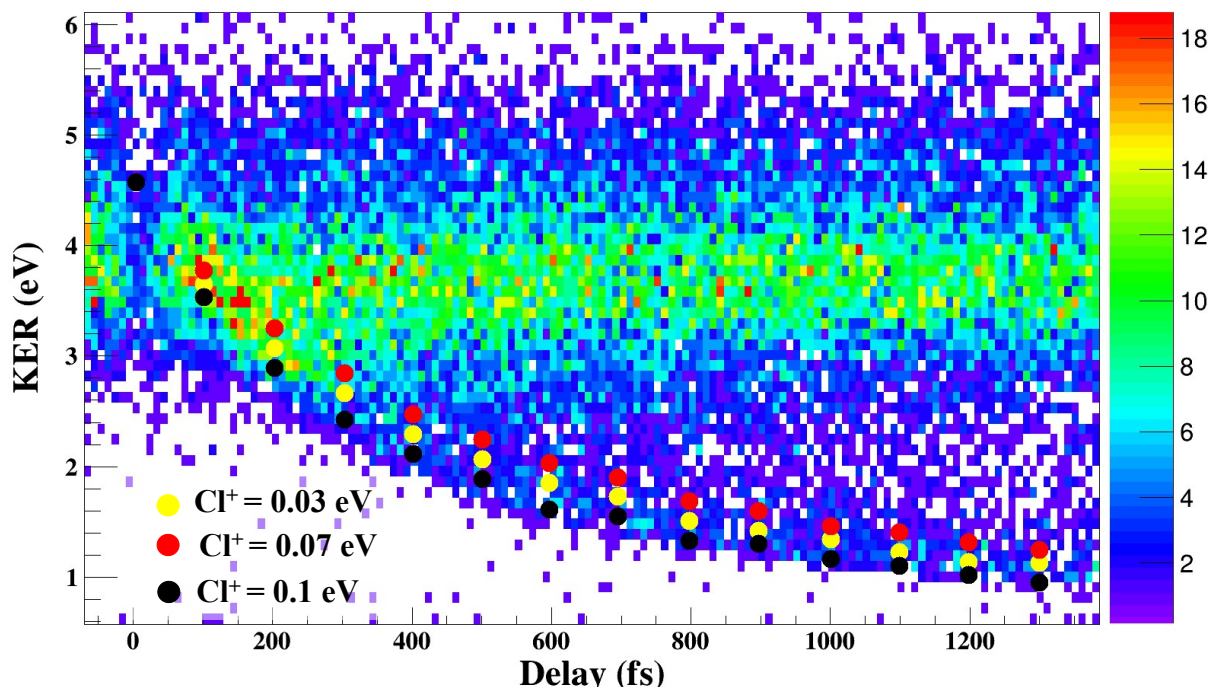


Figure 4.42: Delay-dependent KER distribution for the two-body $\text{CH}_2\text{I}^+ + \text{Cl}^+$ coincident channel. In this 2D plot, the KER of the coincident channel $\text{CH}_2\text{I}^+ + \text{Cl}^+$ is plotted as a function of delay between the pump and probe pulses. Colored circles represent the simulated KER values at different delays assuming that the pump pulse triggers $\text{CH}_2\text{I} + \text{Cl}^+$ dissociation with the translational energies indicated in the figure. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

Analyses of the measured delay-dependent two-body coincident fragments along with the non-coincident single-particle energy distributions reveal the existence of all major dissociative ionization pathways of CH_2ICl , including the channels stemming from the detachment of chlorine or iodine atoms ($\text{CH}_2\text{I}^+ + \text{Cl}$ and $\text{CH}_2\text{I} + \text{Cl}^+$ or $\text{CH}_2\text{Cl}^+ + \text{I}$ and $\text{CH}_2\text{Cl} + \text{I}^+$). Two exemplary two-body coincident spectra probing the C-Cl and C-I bond cleavage are shown in Fig. 4.42 and 4.43, respectively. In these figures, which show the measured KER as a function of the pump-probe delay for $\text{CH}_2\text{I}^+ + \text{Cl}^+$ channel (Fig. 4.42) and $\text{CH}_2\text{Cl}^{2+} + \text{I}^+$ (Fig. 4.43), we observe the behavior very similar to the corresponding figures in section 4.2 (Fig. 4.20 and 4.23): a pronounced horizontal band at high KERs reflecting the CE

of a bound molecule or molecular ion, and descending structure resulting from dissociating channels induced by the pump. In the $\text{CH}_2\text{I}^+ + \text{Cl}^+$ channel (Fig. 4.42), the descending band reflecting Cl detachment is less distinct, and the region between the horizontal and descending features is filled with CE events, indicating that a variety of slow dissociation channels are present. The spectrum from a triply charged $\text{CH}_2\text{Cl}^{2+} + \text{I}^+$ final state in Fig. 4.43 displays a cleaner low-energy band (marked as 2), reflecting the mixture of $\text{CH}_2\text{Cl}^+ + \text{I}$ and $\text{CH}_2\text{Cl} + \text{I}^+$ pathways). In addition, a descending feature (marked 1) converging to higher KERs of ~ 5 eV is also present, which reflects the CE $\text{CH}_2\text{Cl}^+ + \text{I}^+$ already after the pump.

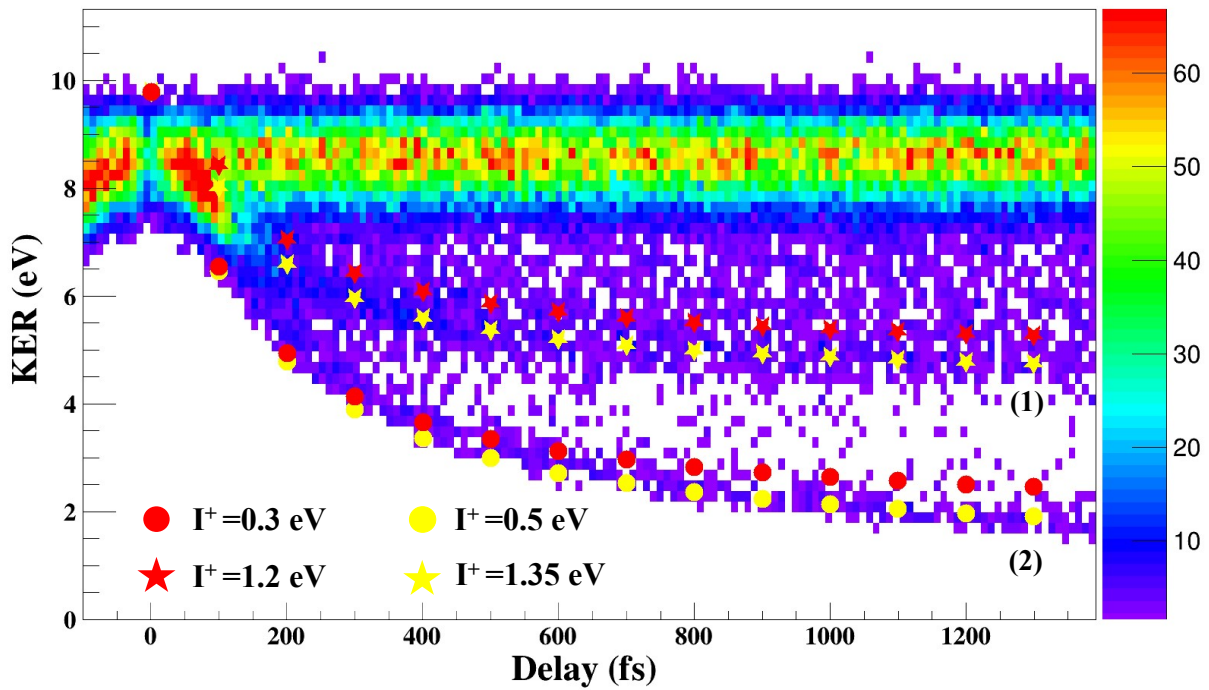


Figure 4.43: Delay-dependent KER distribution for the two-body $\text{CH}_2\text{Cl}^{2+} + \text{I}^+$ coincident channel. In this 2D plot, the KER of the coincident channel $\text{CH}_2\text{Cl}^{2+} + \text{I}^+$ is plotted as a function of delay between the pump and probe pulses. Colored symbols represent the simulated KER values at different delays assuming that the pump pulse triggers $\text{CH}_2\text{Cl} + \text{I}^+$ (circles) or $\text{CH}_2\text{Cl}^+ + \text{I}^+$ (stars) fragmentation channels with the corresponding translational energies indicated in the figure. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

Fig. 4.44 displays the measured delay-dependent KER for $\text{CH}_2^+ + \text{ICl}^+$ channel, which maps the ICl or ICl^+ elimination pathways. The spectrum is rather broad, with both, the

horizontal band at high (4-5 eV) KERs and the descending band propagating to very low KER values visible but diffuse. This suggests a slow ICl ejection with rather broad velocity distribution, consistent with a broad single-particle spectrum of ICl^+ KE shown in Fig. 4.37. Some non-negligible low-energy CH_2^+ events in Fig. 4.37 also suggests the existence of the pathway involving the elimination of the neutral ICl, although we cannot distinguish it from potential three-body dissociation channel yielding CH_2^+ and two neutral halogen atoms, I and Cl.

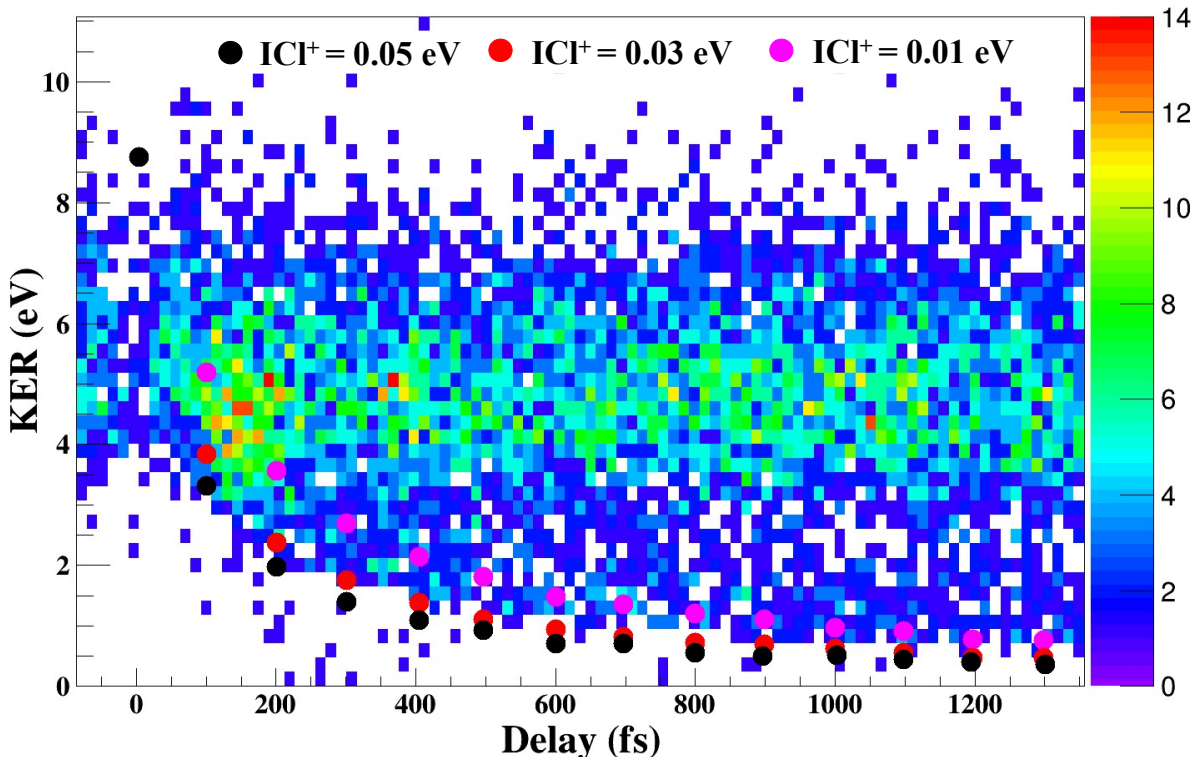


Figure 4.44: Delay-dependent KER distribution for the two-body $\text{CH}_2^+ + \text{ICl}^+$ coincident channel. In this 2D plot, the KER of the $\text{CH}_2^+ + \text{I}_2^+$ coincident channel is plotted as a function of delay between the pump and probe pulses. Colored circles represent the simulated KER values at different delays assuming that the pump pulse triggers $\text{CH}_2 + \text{ICl}^+$ dissociation with the translational energies indicated in the figure. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

Similar to the discussion in section 4.2 for I_2^+ elimination from diiodomethane, ICl^+ can be produced by the combined action of pump and probe pulses, where the pump launches the vibrational wave packet on low-lying ionic states, and the probe projects it onto a higher-lying PES resulting in molecular halogen elimination. In general, oscillatory features that

we observe for different fragmentation pathways of CH_2ICl are rather complex (somewhat similar to the results presented in [68] and will not be discussed here. However, as illustrated in Fig. 4.45 (a), we do observe a clear signature of vibrational motion in the delay-dependent ICl^+ signal. The FFT of this signal shown in Fig. 4.45 (b) displays a clear peak centered at $\sim 140 \text{ cm}^{-1}$, corresponding to the period of $\sim 240 \text{ fs}$. This frequency can be associated with a scissors mode bending vibrations in the low-lying cationic states of CH_2ICl^+ [68] [118] [119]. While it matches closely the value of 144 cm^{-1} that was reported in Ref. [118] for the upper spin-orbit state of the cation, and is further away from the value of $110\text{-}112 \text{ cm}^{-1}$ reported experimentally and theoretically for ionic ground state [68] [120] [119], it is not clear whether this deviation is significant given that the uncertainty in our frequency determination is $\sim \pm 30 \text{ cm}^{-1}$. Nevertheless, the results shown in Fig. 4.45 clearly indicate that ICl^+ elimination is correlated with scissors mode bending vibrations in the ion, and suggest that the maxima of the yield curve in Fig. 4.45 (a) correspond to the times when the ionic wave packet is at its inner turning point.

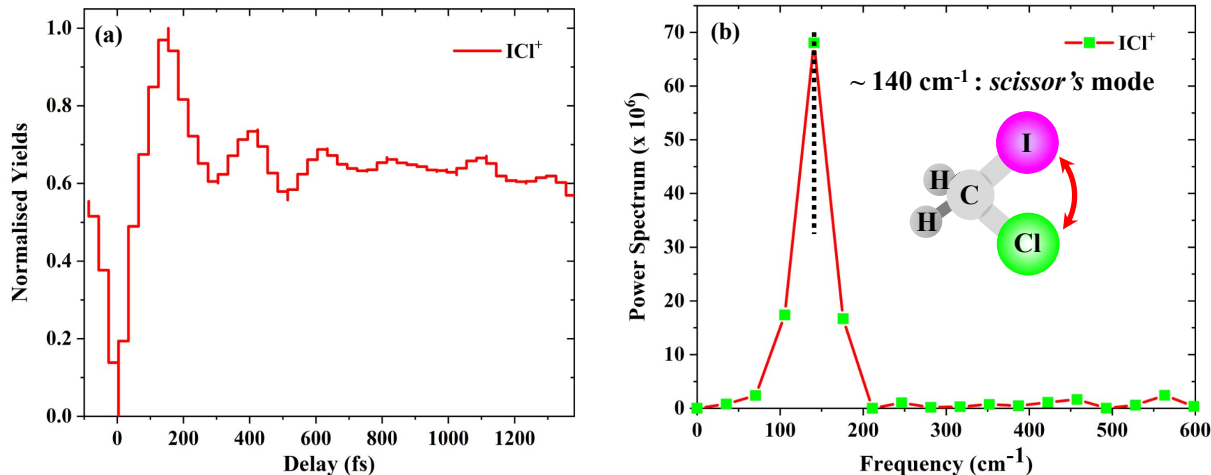


Figure 4.45: (a) The yields of non-coincident ICl^+ ions as a function of pump-probe delay. In this 1D plot, the yield is normalised to 1 with respect to maximum. (b) FFT of the delay-dependent ICl^+ ion yields shown in panel (a). The power spectrum of the FFT signal is plotted along the y-axis, while the frequency values are plotted along the x-axis. Intensity of the laser pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

Imaging ICl elimination and other dissociation channels via three-body Coulomb explosion

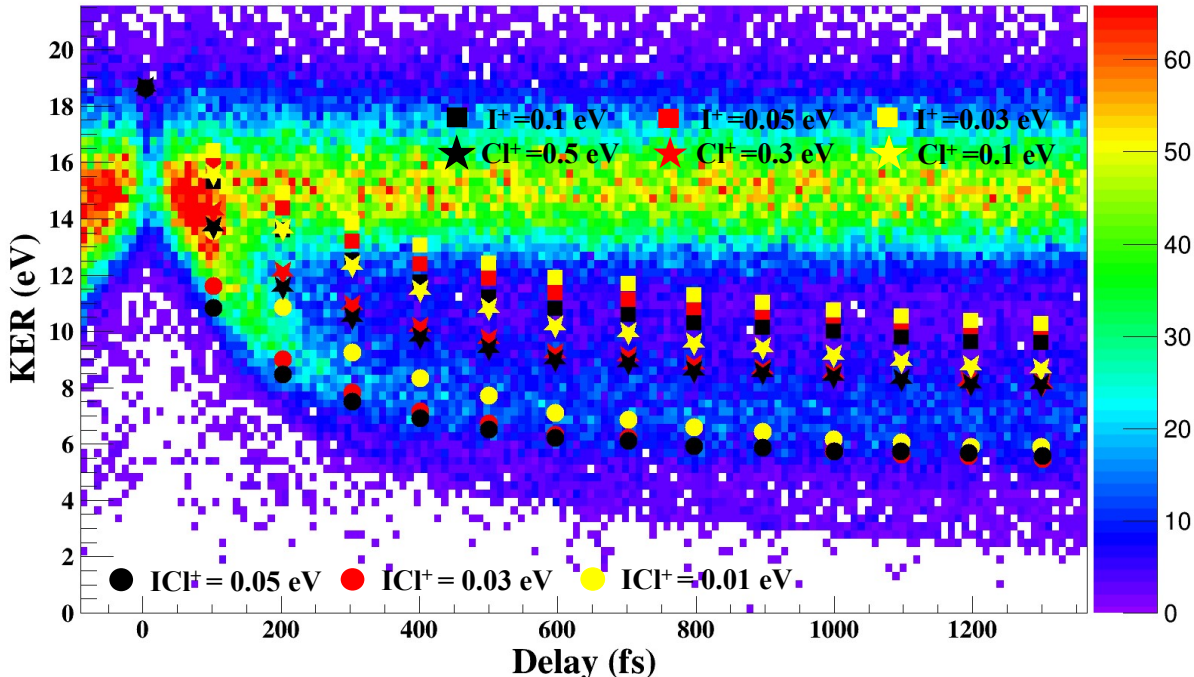


Figure 4.46: Delay-dependent KER distribution for the three-body $\text{CH}_2^+ + \text{Cl}^+ + \text{I}^+$ co-incident channel. Colored symbols represent the simulated KER values at different delays assuming that the pump pulse triggers $\text{CH}_2\text{Cl} + \text{I}^+$ (squares), $\text{CH}_2\text{I} + \text{Cl}^+$ (stars) or $\text{CH}_2 + \text{ICl}^+$ (circles) fragmentation channels with the corresponding translational energies indicated in the figure. Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

In order to get more insight into the details of ICl or ICl^+ elimination and other dissociation pathways of CH_2ICl triggered by intense NIR pulses, we investigate three-body Coulomb explosion patterns of the molecule at different pump-probe delays. We focus on $\text{CH}_2^+ + \text{Cl}^+ + \text{I}^+$ final state, where, as before, we select only the events with ^{35}Cl isotope. We follow all the steps described in section 4.3 for diiodomethane. First, we consider the KER spectrum measured for this channel in Fig. 4.46. The pattern is overall similar to that for CH_2I_2 (see Fig. 4.24), but with larger fraction of events appearing below the most pronounced descending band and converging below 2 eV at large delays. Similar to Fig. 4.24, the most pronounced dissociating band can be reproduced by a CE simulation for molecular halogen elimination channel, while the channels involving atomic halogen detachment fall

into broader descending structure above that most pronounced band. As a next step, we consider a delay-integrated (KER, Θ) map shown in Fig. 4.47, which contains the whole delay range shown in Fig. 4.46 (up to 1400 fs). Similar to the analogous plot for CH_2I_2 (Fig. 4.25), this 2D graph for CH_2ICl displays 3 distinct areas (indicated by dashed region), which reflect the concerted breakup of a bound molecule (1), the sequential fragmentation of metastable intermediates (2), and the CE of dissociating molecules. The latter region appears to be somewhat different from the picture obtained for CH_2I_2 , with much more events at small angles (below 120°). In Fig. 4.48, such (KER, Θ) map is shown for 6 different delays. Similar to the results for CH_2I_2 (Fig. 4.26), a distinct structure shows up at large angles. In addition, a nearly parallel to the first one, but considerably more diffuse feature develops in the lower part of the plot, extending further to smaller angles and smaller KER values than the corresponding CH_2I_2 in Fig. 4.26.

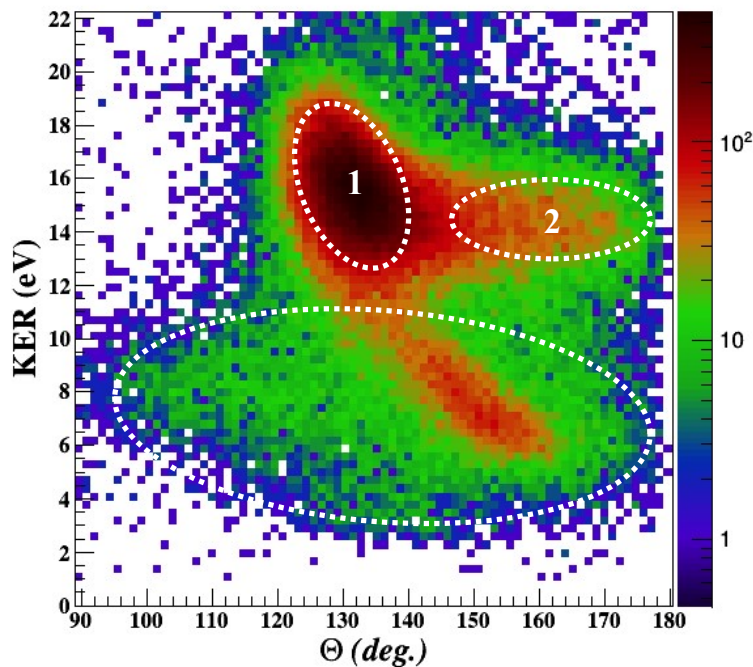


Figure 4.47: Delay-integrated KER- Θ plot for the three-body $\text{CH}_2^+ + \text{Cl}^+ + \text{I}^+$ coincident channel. This 2D plot is integrated from -100 fs to 1.4 ps. In the 2D plot, region (1) corresponds to CE of bound molecule or fragments and the region (2) corresponds to long-lived metastable CH_2I^{2+} and $\text{CH}_2\text{Cl}^{2+}$ ions, and remaining events originate from various dissociating pathways.

Following the procedure developed for CH_2I_2 in section 4.3, to confirm that the distinct

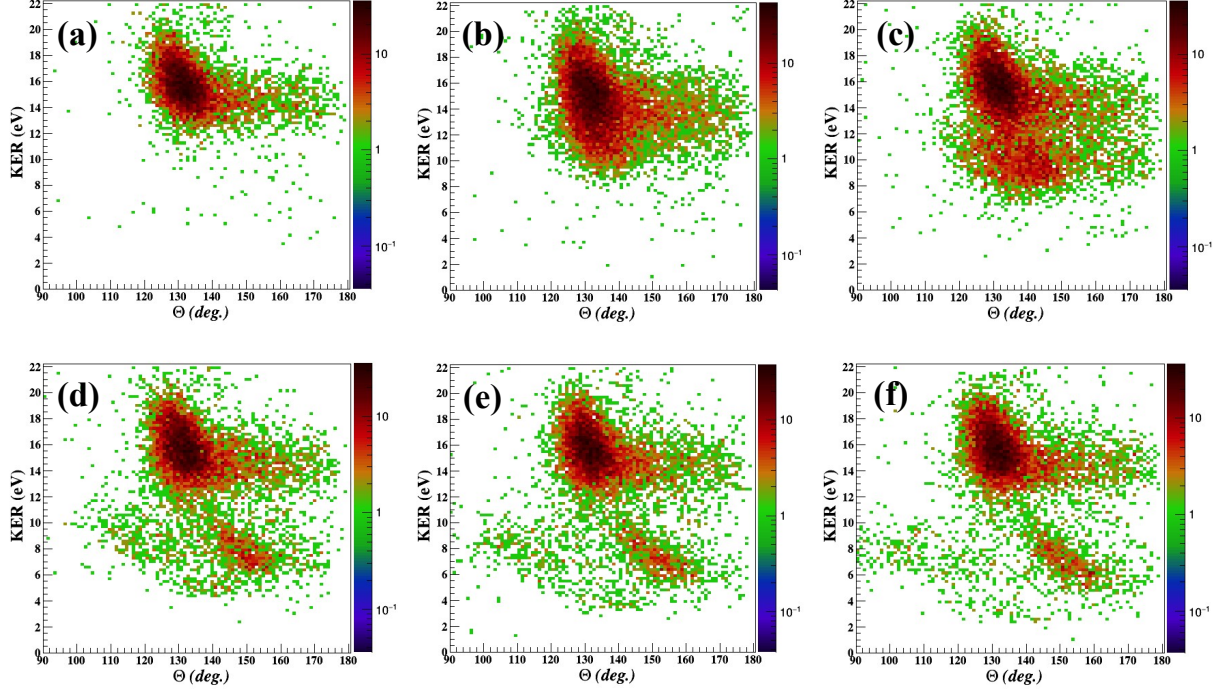


Figure 4.48: KER- Θ plots for the the three-body coincident $\text{CH}_2^+ + \text{Cl}^+ + \text{I}^+$ coincident channel at different delays: (a) $-50 \text{ fs} \rightleftharpoons 50 \text{ fs}$, (b) $50 \text{ fs} \rightleftharpoons 150 \text{ fs}$, (c) $150 \text{ fs} \rightleftharpoons 250 \text{ fs}$, (d) $400 \text{ fs} \rightleftharpoons 500 \text{ fs}$, (e) $700 \text{ fs} \rightleftharpoons 800 \text{ fs}$, and (f) $1.2 \text{ ps} \rightleftharpoons 1.3 \text{ ps}$. Each snapshot is integrated over the corresponding 100 fs delay window.

structure at large angles results from the ICl (or ICl^+) formation, we examine the sum KE

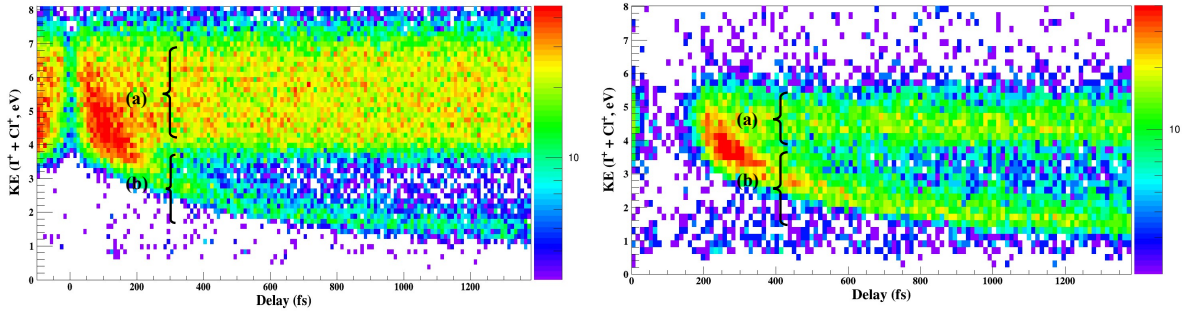


Figure 4.49: Delay-dependent sum KE distribution of three-body coincident Cl^+ and I^+ fragments. On the left side, this distribution is shown for all values of the total KER. A board horizontal band and a descending feature are marked as (a) and (b), respectively. The 2D plot on the right side contains only the events with the total KER $< 12 \text{ eV}$. The high-energy feature refelecting ICl formation is labeled as (a) and the descending band resulting from the detachment of one of the halogen atoms is labeled as (b). Intensity of the pump pulse is kept at $\sim 2 \times 10^{14} \text{ W/cm}^2$ while the intensity of the probe pulse is kept at $\sim 4 \times 10^{14} \text{ W/cm}^2$.

of the two halogen ions (in this case, Cl^+ and I^+) for all events in Fig. 4.49 (a), and for the events with the KER below 12 eV (reflecting dissociating channels) in Fig. 4.49 (b). Similar to CH_2I_2 results in Fig. 4.29, two distinct structure can be seen for the events with $\text{KER} < 12$ eV: one descending to very low energies marked as b), and another one, between 4 and 5 eV, which remains nearly horizontal (marked as a). The events in the upper band originate from ICl elimination channel. Plotting the delay-integrated (KER , Θ) map for the events in that upper band ($3.6 \text{ eV} < \text{sum KE (I, Cl)} < 7 \text{ eV}$, Fig. 4.50 (a)), we observe a clear structure propagating towards 180 degree angle. As can be seen from the figure, this feature can be reasonably well reproduced by the CE simulation assuming ICl / ICl^+ elimination. In Fig.4.50 (b) the events for low KE sum of I^+ and Cl^+ ($< 3.6 \text{ eV}$) are plotted, we observe a broad, slightly tilted structure at 4-10 eV, covering the whole angular range down to 90° degree, and a weaker group of event at higher KERs and angles between 150° and 180° .

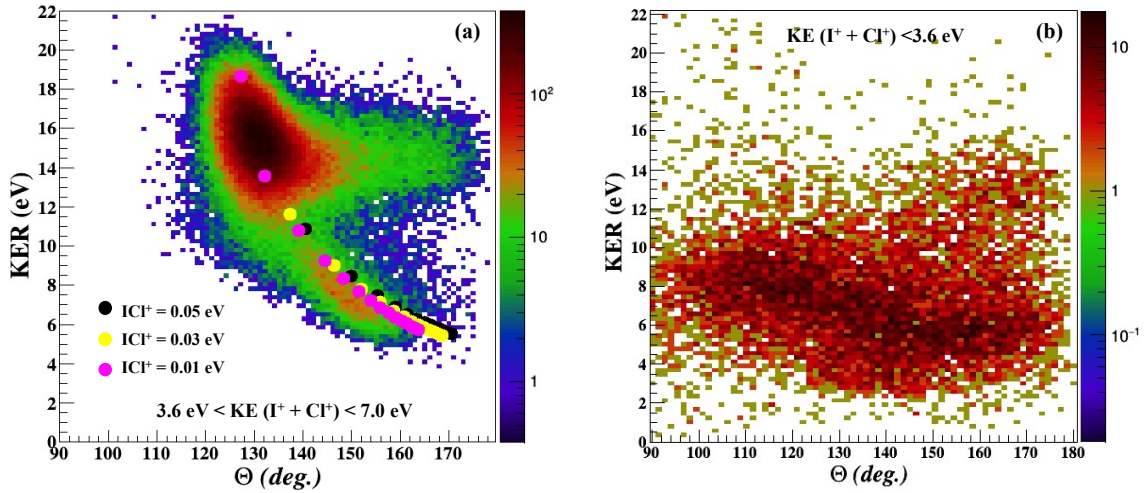


Figure 4.50: KER- Θ plots for the three-body coincident $\text{CH}_2^+ + \text{Cl}^+ + \text{I}^+$ channel for sum KE ($\text{I}^+ + \text{Cl}^+$) conditions. In panel (a), the event with the sum KE ($\text{I}^+ + \text{Cl}^+$) in the range of 3.60 - 7.0 eV are selected. In the panel (b), the sum KE ($\text{I}^+ + \text{Cl}^+$) < 3.60 eV condition is applied. Solid circles represent the simulated values at different delays assuming that the pmp pulse triggers the dissociation in the $\text{CH}_2 + \text{ICl}^+$ fragments, with the translational energies indicated in the figure

To further trace the evolution of all these features, we consider the (KER - Θ) maps with the same conditions on the I^+ and Cl^+ sum KE, but at 10 ps delay. There, the ICl elimination feature in the middle panel (marked as 3) becomes even more localized, while

the contribution from the channels resulting from Cl or I atom (or ion) detachment from the rest of the molecule (marked as 4 in the right panel spreads in angle even more, likely due to CH_2I / CH_2Cl rotation.) The assignment of these two channels, as well as of the delay-independent events for concerted (region 1) or sequential (region 2) breakup can be once again verified by considering Dalitz and Newton plots in Fig. 4.52. Note that the ICl elimination channel (3) contains some small contribution from region (4), appearing on the top of the Dalitz plot and in the middle of the Newton diagram in column (3) of Fig. 4.52.

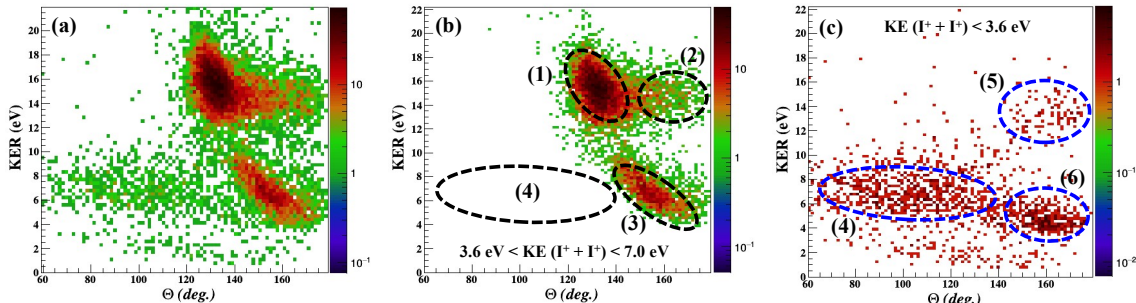


Figure 4.51: KER- Θ plots for the three-body coincident $\text{CH}_2^+ + \text{Cl}^+ + \text{I}^+$ channel for different sum KE ($\text{I}^+ + \text{Cl}^+$) conditions at 10 ps. Here, panel (a) includes all events, whereas panels (b) and (c) contains the events with the sum KE ($\text{I}^+ + \text{Cl}^+$) between 3.6 and 7.0 eV, and below 3.6 eV respectively.

Besides the channels discussed above, the (KER- Θ) map at 10 ps filtered on low KE sums of Cl^+ and I^+ contains three additional features. First, there is a structure marked (5) at large angles and small KERs, very similar to the one for CH_2I_2 in Fig. 4.32 (d), which we assumed to originate from metastable I_2 intermediates decaying on ps time scale. We speculate that the same feature in CH_2ICl experiment results from similar process involving ICl decay. Second, a weak but distinct structure appears at large KERs close to 180° (marked 6). While we assigned an analogous feature in CH_2I_2 to the CE of the molecule ($\text{CH}_2\text{I}^+ + \text{I}^+$) by the pump pulse, here, we cannot make a reliable assignment. However, we speculate that these events also originate from one of the CE channels triggered by the pump pulse. Finally, a diffuse band below 2 eV starts to be visible in 10 ps data of Fig. 4.51. The only channel which can result in such low KER values for triply charge three-body CE is the three-body dissociation after the pump, such that at large delays all interatomic distances become large, and the effect of Coulomb repulsion is negligible.

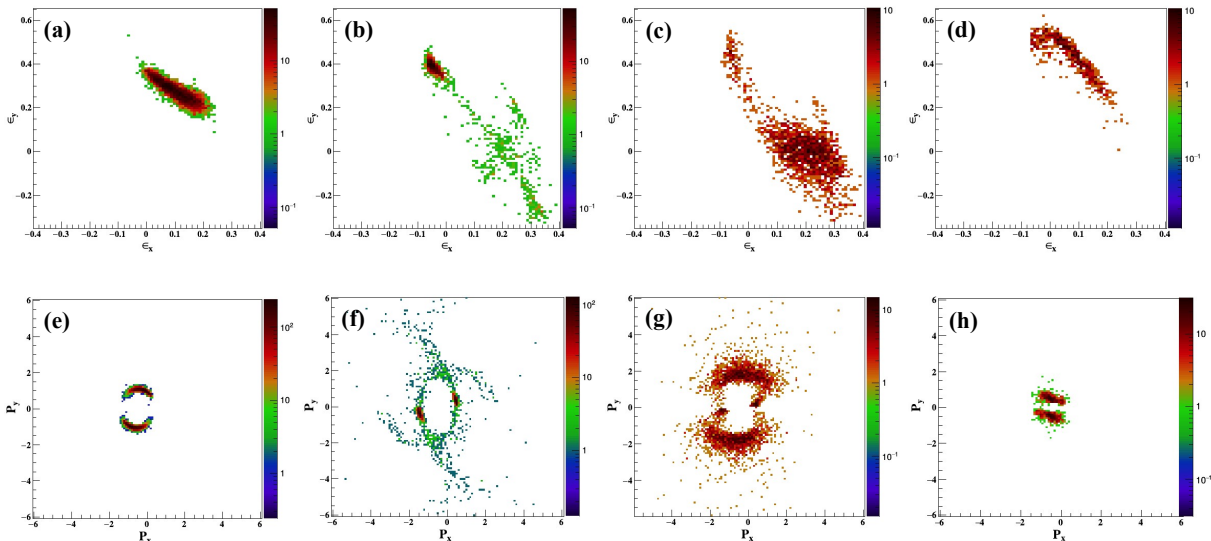


Figure 4.52: Dalitz and Newton plots for the different regions of KER- Θ plot of three-body coincident $\text{CH}_2^+ + \text{Cl}^+ + \text{I}^+$ channel at 10 ps. Here, panels (a) to (d) in upper row are the Dalitz plots for the corresponding KER- Θ regions numbered as (1) to (4) in 4.51. Similarly, panels (e) to (h) in lower row are the Newton diagrams for the corresponding KER- Θ regions (1) to (4) in 4.51.

Finally, applying the conditions on the sum KE of I^+ and Cl^+ discussed above, we plot a series of snapshots detailing $\text{ICl} / \text{ICl}^+$ elimination in 50 fs steps in Fig. 4.53. There, similar to CH_2I_2 case, the direct formation of the ICl product “departing” from the main spot within the first 100 fs can be traced. Interestingly, there is also a group of events descending from ~ 15 eV at large angles, which becomes clearly visible in snapshots (4) and (5) (~ 150 -200 fs), and later merges with the direct ICl production channel. This pathway might reflect an alternative ICl formation pathway, although at the moment, we do not have a clear picture for this.

4.5 Summary and discussion

In the above four sections, we described a detailed experimental study of strong-field driven dynamics in two di-halomethanes. In both molecules, we observed a clear correlation between different dissociative ionization pathways, in particular, molecular halogen elimination, and the large-scale bending vibrations of the molecule. We then focused on the analysis of tran-

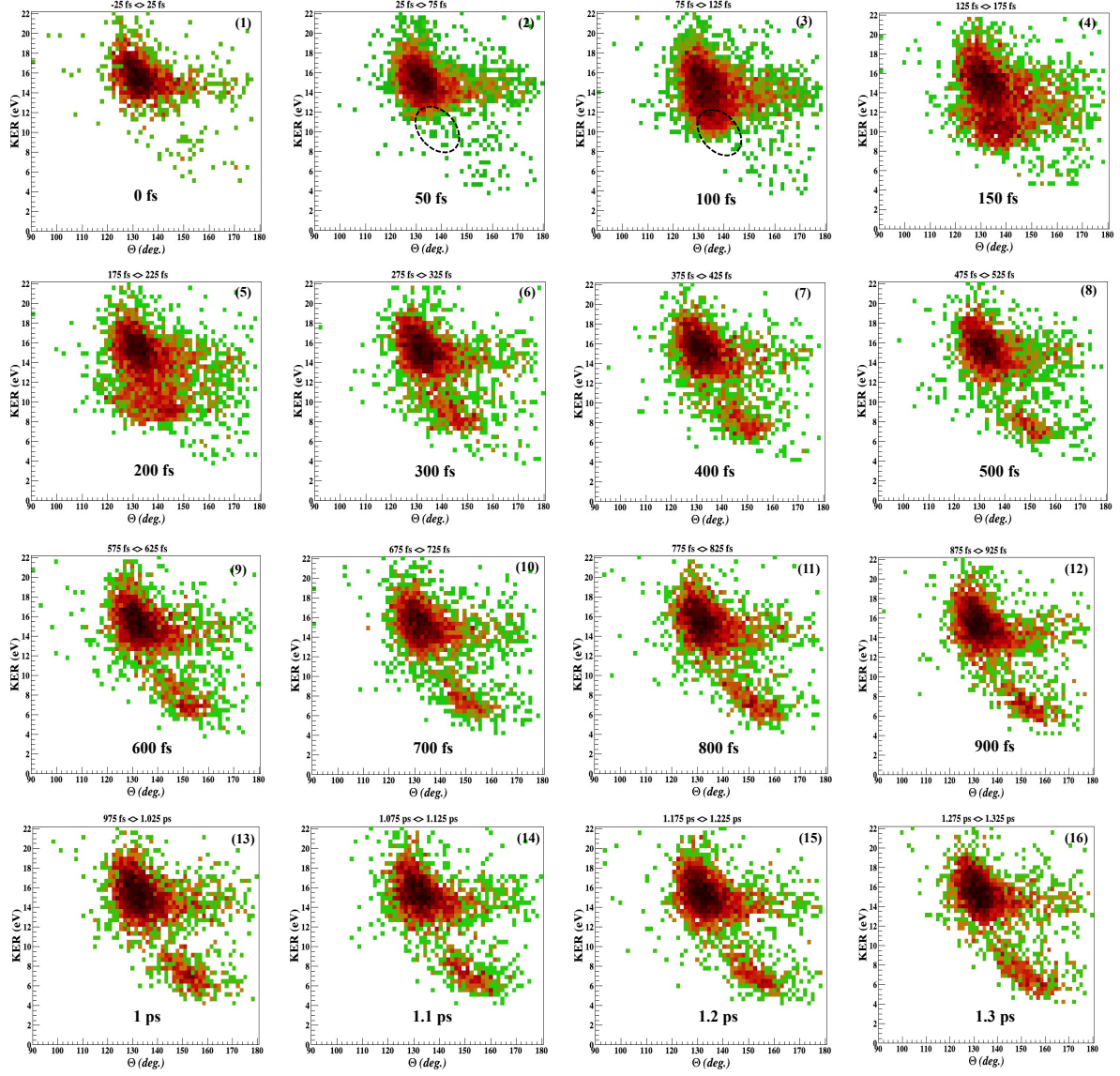


Figure 4.53: KER- Θ plots for the three-body coincident $\text{CH}_2^+ + \text{Cl}^+ + \text{I}^+$ channel involving ICl formation channels. There are 16 snapshots numbered from (1) to (16), and each snapshot corresponds to the 50 fs delay window centered at the values shown in the figure.

sient molecular geometries created after the interaction with an intense NIR pulse probed via three-body Coulomb explosion. In this analysis, we clearly identified signatures of molecular halogen elimination, and experimentally disentangled it from the other dissociation channels. Our data strongly support direct, “synchronous” molecular halogen formation as a main elimination mechanism, although certain contributions from the complimentary pathways cannot be excluded. In particular, the group of events appearing at large angles close to 180° , propagating downwards with the increasing delay, and finally merging with the direct elimination pathway, can be traced in Fig. 4.53 for CH_2ICl . Similar (although much weaker) feature can be traced in Fig. 4.34 for CH_2I_2 as well. Although the assignment of these events is not clear, one possibility would be ICl or I_2 elimination from the isomerized geometry. In our present analysis we can neither confirm nor reject the contribution from the isomerization pathway. The reason for this is that, as can be seen in Fig. 2.15, the CE at the isomer geometry is expected to generate events in the region of our $(\text{KER}-\Theta)$ map covered by the strong feature resulting from sequential breakup via long-lived metastable intermediates. We will discuss possible ways to circumvent this issue in the next Chapter.

The approach employed in this work is very sensitive to nuclear geometry of a molecule. However, our three-body analysis is rather insensitive to the electronic or even charge state of a particular intermediate fragment. In the specific example of I_2 or ICl elimination, from our 2D patterns, we do not know in which charge state the molecular halogen is created. From single-pulse TOF spectra we know that there is a certain amount of I_2^+ or ICl^+ ions created after the pulse. However, given the rather low branching ratios of these ions to the other fragments (in particular, resulting from the detachment of a single halogen atom or ion), it does not appear likely that these ionic elimination channels can be responsible for all molecular halogen events that we observe in our three-body CE patterns. A large amount of low-energy CH_2^+ ions and their strong correlation with the scissors-mode bending vibration also hint that a significant amount of molecular halogen is produced in a neutral state. However, in order to prove it experimentally we would need a more reliable and systematic way to compare the ion branching ratios in different charge states, and / or an independent tool for the characterization of the electronic state of a fragment molecule.

Besides the Coulomb explosion imaging, we have also traced the dynamics of molecular halogen elimination observing I_2^+ or ICl^+ as a final state in a pump-probe experiment. Using channel-and energy-resolved Fourier analysis, we have shown that it is rather sensitive to the I-C-I or I-C-Cl angle at the moment when the probe pulse arrives. Depending on the dominant dissociation and ionization pathways, it can also be sensitive to stretching vibrations, and can probe the wave packet motion either in ionic or in the neutral ground states.

Chapter 5

Imaging photochemical dynamics in diiodomethane driven by UV light

5.1 Objectives and scope

In the previous Chapter, we analyzed basic features of strong-field interactions with two di-halomethane molecules at NIR wavelengths, and developed a detailed step-by-step imaging scheme based on CE resulting from such interaction. In this Chapter, we discuss the application of this approach for probing photochemical processes induced by UV light. Our main goal here is to disentangle and characterize basic UV-induced reactions discussed in section 2.2. Practically, we have performed a series of experiments very similar to those described in section 4.2-4.4, with very similar probe pulses and identical probing scheme. The major difference is the use of a much weaker UV pulse at three times higher individual photon energy as a pump. In addition, we used slightly more intense probe pulses than in the NIR-NIR pump – probe experiments (5×10^{14} W/cm² instead of 4×10^{14} W/cm²). This difference, which might appear minor, allowed us to probe the photochemical dynamics via CE to higher charge states, up to 5+. Besides general considerations discussed in sections 2.3 and 2.5, this possibility provides a major advantage here. As discussed in relation to Fig. 4.10, where the same high intensity was used for a single pulse measurement, the plot

depicting the measured KER as a function of the angle between the momenta of two iodine ions for the five-fold charged $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ channel in Fig. 4.10 (c) does not contain any contribution from the sequential fragmentation of long-lived metastable intermediates, [72] which hinder the observation of the events at high KER and large angles for lower charge states, as can be clearly seen in Fig. 4.10 (a,b). And it is in this region where, according to the CE simulation discussed in section 2.5, we expect the contributions from the isomerized $\text{CH}_2\text{I-I}$ geometries (see Fig. 2.15).

The intensity of $5 \times 10^{14} \text{ W/cm}^2$ was the highest value we could use in our experiments while still maintaining the condition of less than one fragmentation event per laser shot, which is a necessary condition for coincident measurements. At the same time, this value was just above the threshold intensity for producing the five-fold charged state of a molecule. Unfortunately, we could not employ the intensity higher than $\sim 4 \times 10^{14} \text{ W/cm}^2$ in NIR-NIR pump-probe experiments on dihalomethanes, and that was not high enough to collect reasonable statistics for $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ channel. Two limitations precluding this were (1) too high optical intensity in the overlap region (which already caused issues close to zero delays in CH_2ICl measurement) and (2) insufficient contrast of the pump-probe experiment in a single-color scheme, where both, the pump and the probe have the same wavelengths and produce similar fragments. Both of these limitations are lifted in the UV-NIR pump-probe experiment. Accordingly, we employed highest possible probe intensity and mainly focused on the analysis of $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ channel. Since the pulse duration of our UV pulses (with the wavelength centered at 263.5 nm) is 40-45 fs FWHM (see Fig. 3.4), as compared to 25 fs NIR pulses, temporal of the measurements described in this chapter is ~ 50 fs, and is somewhat worse than for NIR-NIR experiments. Nevertheless, as will be detailed in the following, it is sufficient to resolve most processes of interest.

5.2 CH_2I_2 molecule under single UV pulses

Since the main goal of this part is to elucidate single-photon driven dynamics, UV pulse intensity was kept moderate. However, given a moderate CH_2I_2 absorption cross section ($\sim$

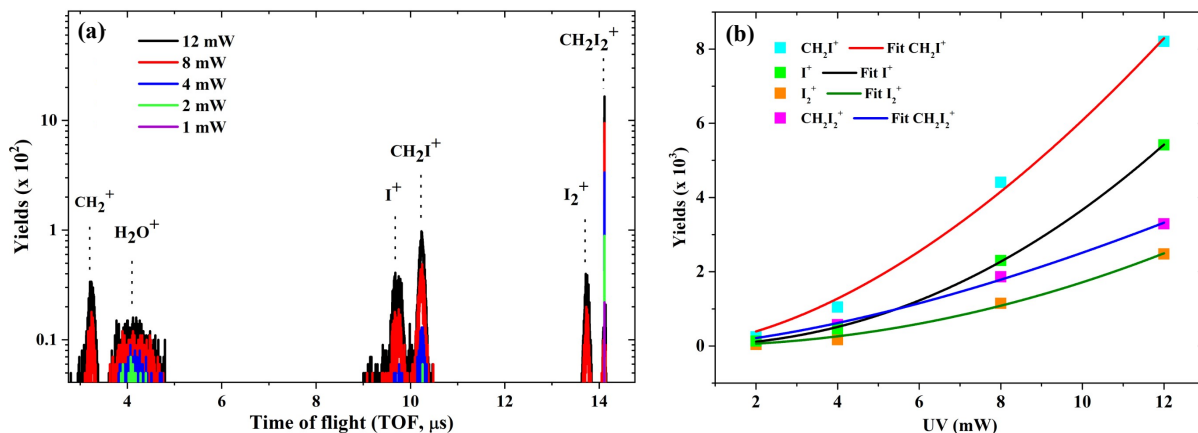


Figure 5.1: (a) Ion time of flight (TOF) spectrum from the ionization of CH_2I_2 by a single UV pulse at different powers. 1 mW corresponds to the peak intensity of $\sim 2 \times 10^{12} \text{ W/cm}^2$. (b) Yield of dominant ionic fragments as a function of UV power. Solid lines show the power fits of the corresponding ion yield curves (see text).

1.5 MB at our central wavelength), in order to observe noticeable time-dependent changes, we need to keep the photon fluence of the pump pulse rather high, such that two- or three-photon absorption cannot be avoided. Correspondingly, even though the main effect of the UV pump pulse excitation should be the excitation in the neutral molecule, which cannot be directly detected in a single-pulse experiment using our technique, we do observe a non-negligible amount of UV-induced ionization and dissociative ionization. To get a more quantitative idea about the level of ionization and the resulting ionic fragments, we perform a series of single-pulse measurements as a function of UV pulse power. The measured ion TOF spectra are plotted in Fig. 5.1 (a), whereas the yield of individual ions as different UV pulse powers is depicted in Fig. 5.1 (b). According to our beam parameter measurements, the UV power of 1 mW ($0.1 \mu\text{J}$ per pulse at 10 kHz) corresponds to $\sim 2 \times 10^{12} \text{ W/cm}^2$, such that the highest UV intensity used here is $\sim 2.4 \times 10^{13} \text{ W/cm}^2$. Besides the water peak from the residual gas and the parent ion signal, all four major dissociative ionization products of CH_2I_2 (CH_2I^+ , I^+ , I_2^+ , CH_2^+) appear in the spectrum at the highest UV power, whereas at the lowest value, only the parent ion is detectable above the noise level. Within the validity of the low-order perturbation theory, for the absorption of n photons, the ionization yield is expected to be proportional to I^n , and, for fixed pulse parameter, to P^n , where I is the light intensity and P – average pulse power shown in Fig. 5.1. This is supposed to hold if

neither of photoabsorption steps is saturated. Fitting the yield curves in Fig. 5.1 (b) with a function $Y = aP^n$, we obtain the following values of n : 1.72 ± 0.13 for CH_2I^+ , 2.14 ± 0.05 for I^+ , 2.05 ± 0.16 for I_2^+ and 1.55 ± 0.08 for the parent ion (CH_2I_2^+). This observation can be rationalized using the appearance energies for different ions given in Table 2.1 and the photon spectrum shown in Fig. 2.2 and Fig. 3.3. While the production of any fragment ion requires the absorption of at least three photons, the ionization threshold for parent ion can be reached already by absorbing two photons from the blue part of our UV spectrum. At the central wavelength, or in the red part of the spectrum, one does require three photons to be absorbed for ionization. The power of ~ 2 instead of 3 for fragment ions is most likely due to the saturation of the first photoabsorption steps. With our beam parameters, and assuming the absorption cross section of 1.5 MB (taken from [44]), the photoabsorption is supposed to approach saturation at 4-5 mW. The lower value observed for the parent ion reflects the mixture of two- and three-photon absorption processes.

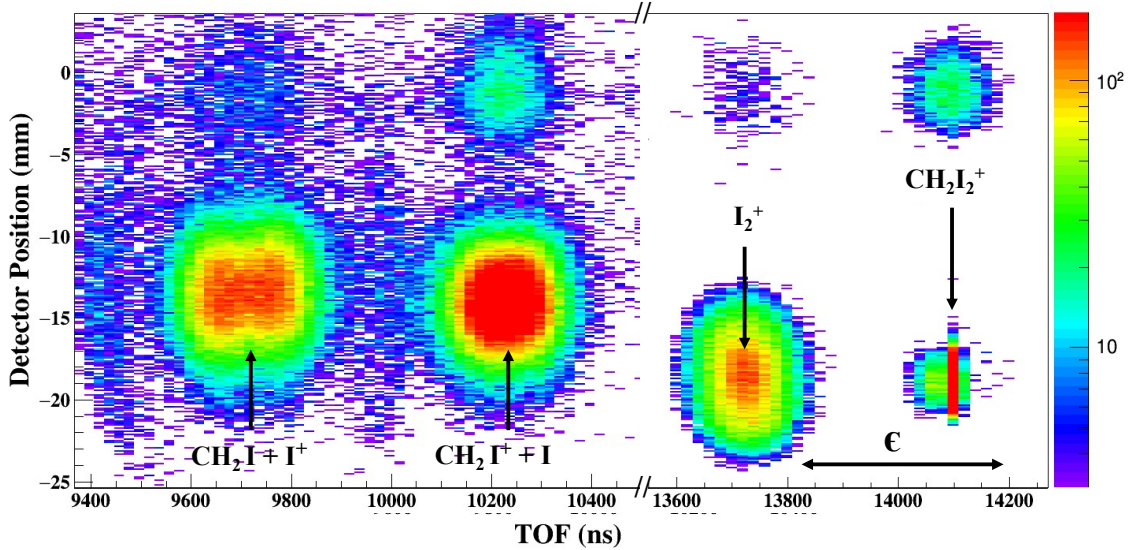


Figure 5.2: Ion time of flight (TOF) spectrum as a function of ion hit position at the detector after the ionization of CH_2I_2 by a single UV pulse. The spectrum is zoomed into two areas, displaying the TOF regions containing I^+ and CH_2I^+ ions on the left, and I_2^+ and CH_2I_2^+ ions on the right. The intensity of the UV pulse is kept at $\sim 10^{13} \text{ W/cm}^2$.

As illustrated in Fig. 5.2 and 5.3, all fragment ions are predominantly produced with low KE. In Fig. 5.2, which displays the measured TOF spectrum as a function of the hit position on the detector (reflecting the rescaled momentum distributions of the ions), the

events appear as rather localized structures peaked in the middle, in stark contrast to the NIR data presented in Fig. 4.2. Correspondingly, the fragment ion KE distributions shown in Fig. 5.3 are dominated by the very low-energy ions, with the only exception of a weak shoulder in the I^+ KE spectrum at $1.5 - 2$ eV (middle panel of Fig. 5.3). Since we did not detect any coincidence events in UV-only experiments, we assume that this feature results from one of the energetic dissociative ionization pathways. No doubly charged ions have been detected in the spectra. In the pump-probe experiments described below, a fraction of ions generated by UV-pump is very small compared to those produced by the NIR probe.

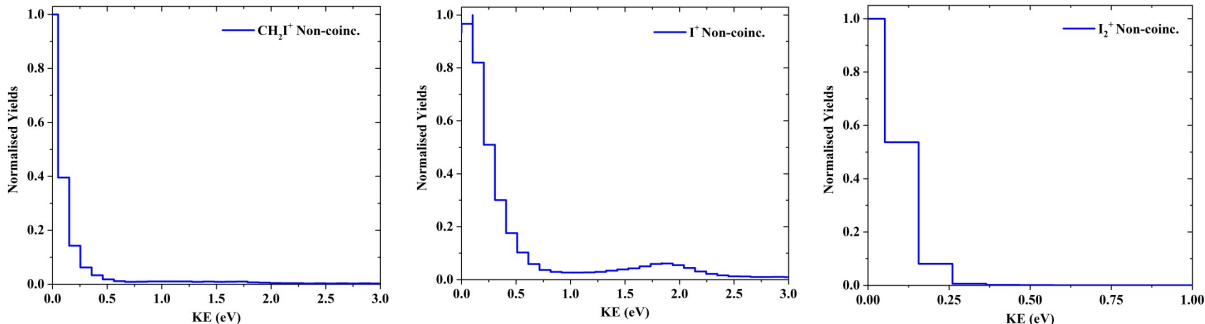


Figure 5.3: Kinetic energy (KE) distribution of CH_2I^+ , I^+ , and I_2^+ fragments after CH_2I_2 ionization by a single UV pulse at the intensity of $\sim 10^{13}$ W/cm².

5.3 Mapping UV-driven photodissociation of CH_2I_2 with two-body Coulomb explosion

In the following sections, we will discuss the results of UV pump – NIR probe experiments on diiodomethane. In all of these experiments, the NIR probe pulses of 25 fs duration, ~ 790 nm central wavelength and intensity of 5×10^{14} W/cm² has been used. The intensity of the UV pump pulse was varied between 2×10^{12} W/cm² and 2×10^{13} W/cm² (1 mW and 10 mW average UV power, respectively). In order to increase the pump-probe contrast, in most of the cases it was set to the latter value. Several dedicated scans at different UV powers have been carried out in order to identify contributions from two- and multiphoton absorption processes.

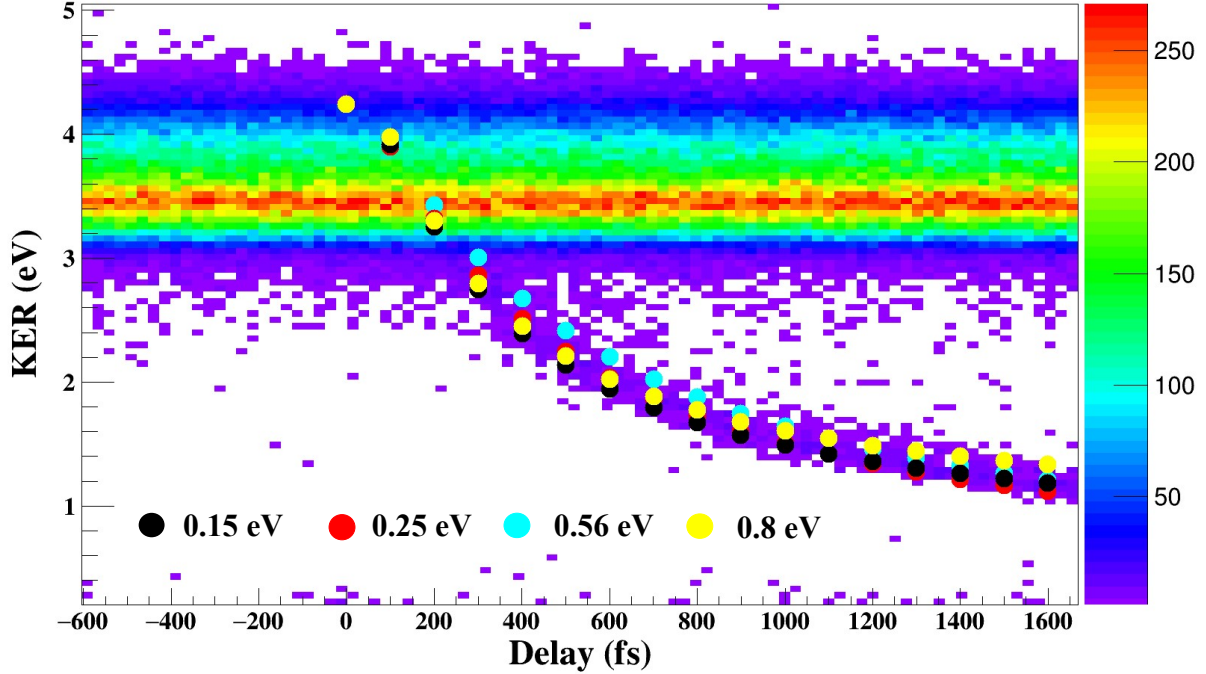


Figure 5.4: Delay-dependent kinetic energy release (KER) for the two-body $\text{CH}_2\text{I}^+ + \text{I}^+$ coincident channel after UV pump and NIR probe pulses. In this 2D plot, the KER of the $\text{CH}_2\text{I}^+ + \text{I}^+$ coincident channel is plotted as a function of delay between the UV and NIR pulses. Solid circles represent the simulated KER values at different delays assuming different asymptotic dissociation energies as indicated in the figure. Intensity of the UV pulse is kept at $\sim 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

In this section, we focus on the events ending up in two-body CE explosion of a molecule after the interaction with the probe pulse. Correspondingly, it mainly addresses two-body dissociation dynamics triggered by the pump. In Fig. 5.4, a KER distribution measured for coincident pairs of CH_2I^+ and I^+ fragments is shown as a function of UV-NIR delay. A spectrum is in general similar to a series of such delay-dependent maps shown in Chapter 4, with a horizontal high-energy band and descending band reflecting the dissociation induced by the pump. However, because of well-defined energy transfer by a single UV photon (in contrast to broad energy distributions characteristic for multiphoton for strong-field induced processes), the dissociation band in Fig. 5.4 is much cleaner, and more localized than most of the patterns discussed in the previous chapter. We compare the time evolution of this structure with the prediction of a CE simulation, which relies on the KERs measured for

the same channel at 10 ps and 20 ps delays (shown in the figure) for the determination of translational velocity of the dissociation reaction. In accordance with the considerations presented in the previous Chapter, the simulation overestimates the measured KER of the fragments at small delays (small internuclear separations), but describes the experiment pretty well at the delays larger than ~ 250 fs. The non-Coulombic nature of the final dicationic states is the main reason for discrepancy at small delays.

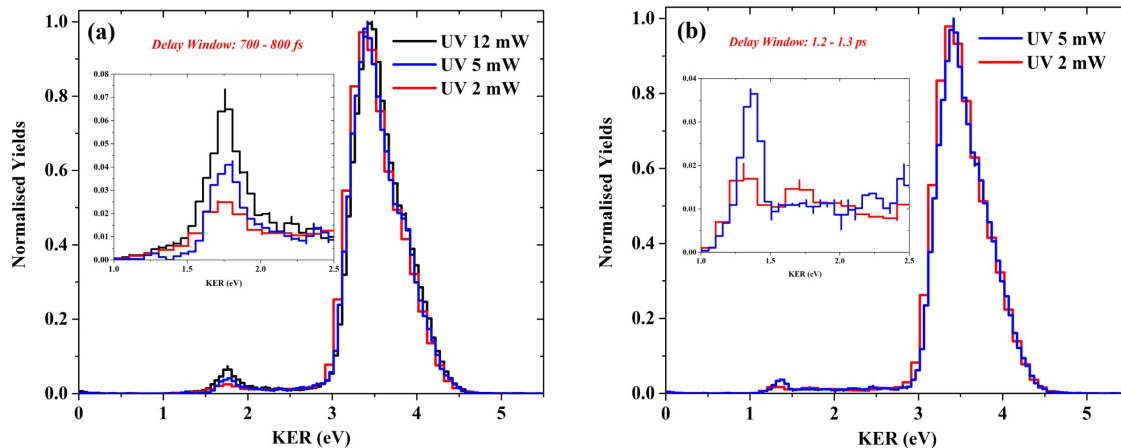


Figure 5.5: Kinetic energy release (KER) for the two-body $\text{CH}_2\text{I}^+ + \text{I}^+$ coincident channel in the delay window 700-800 fs and 1.2-1.3 ps. In this 1D plot, the KER of the $\text{CH}_2\text{I}^+ + \text{I}^+$ coincident channel is plotted for different power of the UV pump pulse. The yields of the coincident channels is normalised to 1 with respect the Coulomb exploded fragments by NIR pulses. Intensity of UV pump pulse is kept $\sim 2 \times 10^{12} - 2.3 \times 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

In order to verify that the dissociation feature in Fig. 5.4 indeed originate from single UV-photon absorption, in Fig. 5.5 we plotted the measured KER distributions in two fixed delay regions for different UV pulse intensities. These spectra are normalized to the maximum of the delay-independent band between 3 and 4.5 eV. The dissociation channel appears as a small peak at 1.5 – 2 eV in Fig. 5.5 (a) (700-800 fs), and between 1 and 1.5 eV in Fig. 5.5 (b) (1.2 – 1.3 ps), and its enlarged view is shown in the inset in each panel. The integrated yield of this peak scales linearly with the UV pulse power, suggesting that single-photon absorption is indeed a dominating mechanism, resulting in CH_2I_2 dissociation into $\text{CH}_2\text{I} + \text{I}$ or $\text{CH}_2\text{I} + \text{I}^*$.

A complementary view of this dissociation channel can be obtained by the CE of higher

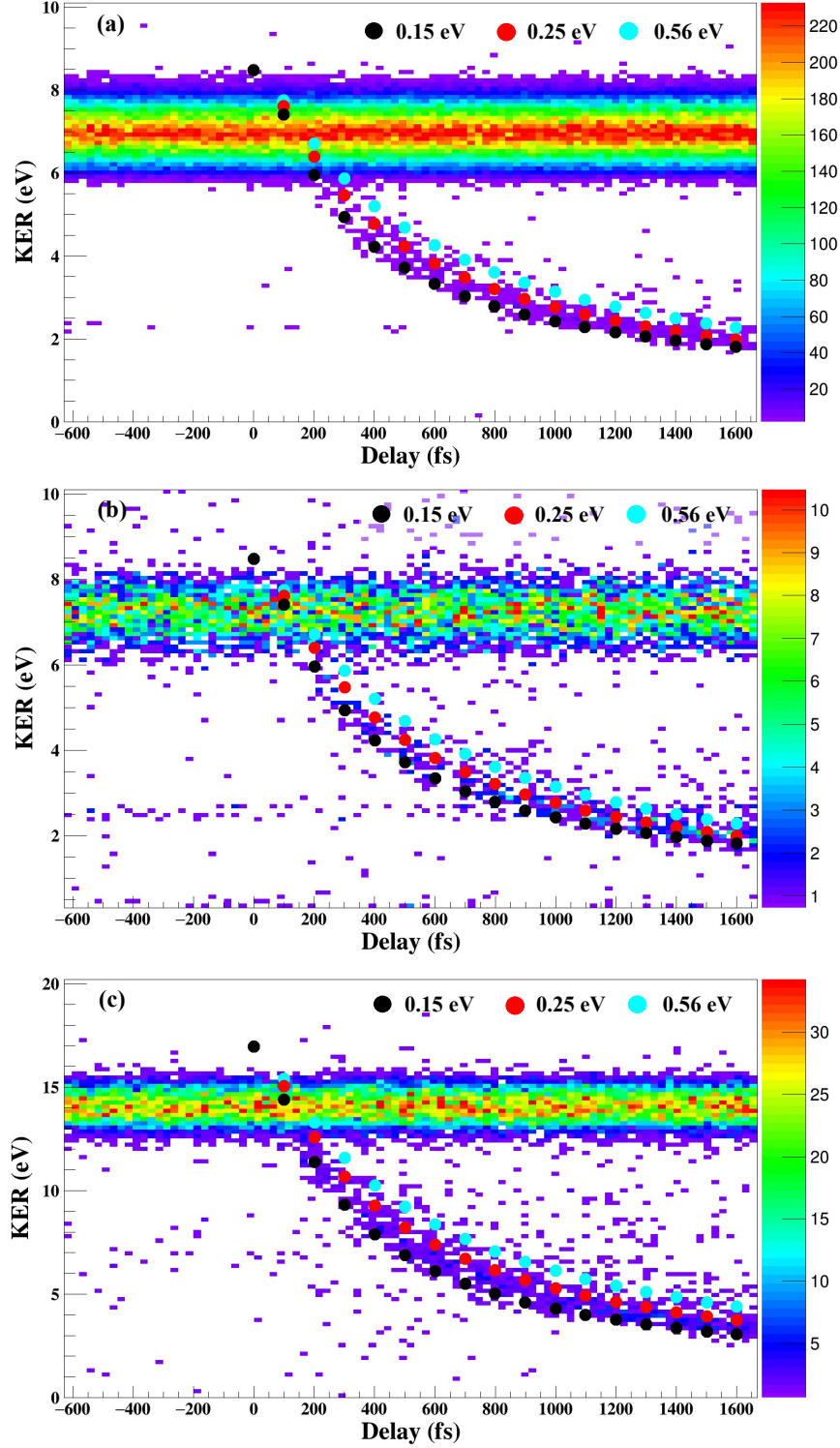


Figure 5.6: Delay-dependent kinetic energy release (KER) for three different two-body coincident channels after UV pump and NIR probe pulses: (a) $\text{CH}_2\text{I}^{2+} + \text{I}^+$, (b) $\text{CH}_2\text{I}^+ + \text{I}^{2+}$, and (c) $\text{CH}_2\text{I}^{2+} + \text{I}^{2+}$. Solid circles represent the simulated KER values at different delays assuming different asymptotic dissociation energies as indicated in the figure. Intensity of UV pump pulse is kept $\sim 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

charge states. It is illustrated in Fig. 5.6 for $\text{CH}_2\text{I}^{2+} + \text{I}^+$ (a), $\text{CH}_2\text{I}^+ + \text{I}^{2+}$ (b) and $\text{CH}_2\text{I}^{2+} + \text{I}^{2+}$ (c) final state. Each of these spectra manifest a pronounced and well-defined signature of the dissociation channel, which is modelled well by the CE simulation with the same set of asymptotic energies as in Fig. 5.4. The dissociating band in all of the maps shown in Fig.5.6 falls between the simulated curves employing the limits of 0.15 eV and 0.56 eV translational energies, while the maxima of our asymptotic distribution at 20 ps (not shown here) are located at 0.25 eV and 0.4 eV. Given the limits of our KER resolution and rather broad energy bands in CH_2I_2 , this is in a very good agreement with previously reported translational energies of 0.35 eV and 0.4 eV for $\text{CH}_2\text{I} + \text{I}^*$ and $\text{CH}_2\text{I} + \text{I}$ channels, respectively [44]. Since at our photon energy, the access energy above the dissociation limit for these two channels is estimated to be 1.56 eV and 2.5 eV [44], this means that $\sim 80\%$ of this energy goes into internal degrees of freedom. In particular, it can manifest itself in CH_2I rotation, as will be discussed in the next section.

5.4 Imaging photochemical processes in CH_2I_2 with three-body Coulomb explosion

General overview

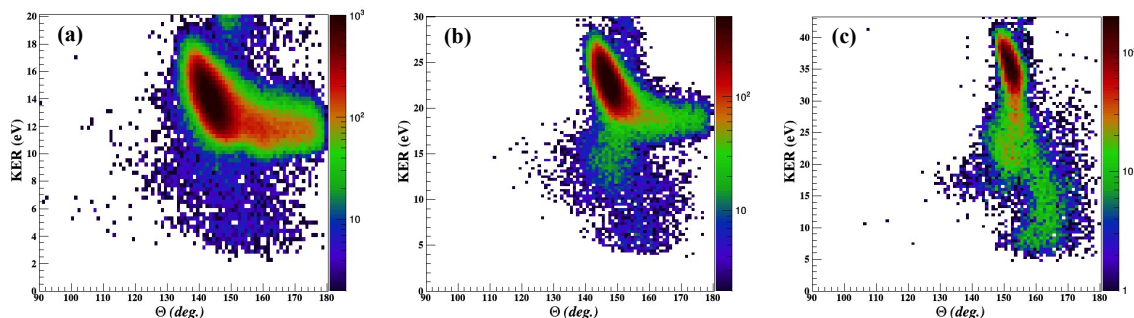


Figure 5.7: KER- Θ plots for the three-body coincident channels in three different final charge states after UV pump and NIR probe pulses. These plots are integrated over the delay range from 0 to 850 fs. (a) $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$, (b) $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^+$, and (c) $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$. Intensity of UV pump pulse is kept $\sim 10^{13}$ W/cm² while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14}$ W/cm².

As discussed in Chapter 4, two-body CE imaging does not provide direct information on intermediate geometries of polyatomic molecules, beyond the length and spatial orientation of the bond which breaks. However, such information can be obtained using three-body CE, as discussed in sections 4.3 and 4.4. Here, we follow the same procedures to visualize and disentangle the reaction pathways triggered by the interaction with UV light. We start with a general overview of KER vs. angle maps introduced in Chapter 4. In Fig. 5.7, the KER spectrum integrated over the delay range from 0 to 850 fs is shown as a function of the angle Θ between the momentum vectors of the two iodine for three different final charge states ($\text{CH}_2^+ + \text{I}^+ + \text{I}^+$, $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^+$ and $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ channels in (a), (b), and (c), respectively). In general, the spectra resemble those obtained in NIR-NIR experiments (see Fig. 4.25 and Fig. 4.47) for triply-charged state, while the upper part is rather similar to such 2D spectrum for a corresponding charge state obtained with a single NIR pulse of the same intensity (Fig. 4.10). Noticeably, here we have acquired a statistically significant data set on $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$, which carry clear signatures of two-pulse effects at low KERs. As discussed in Section

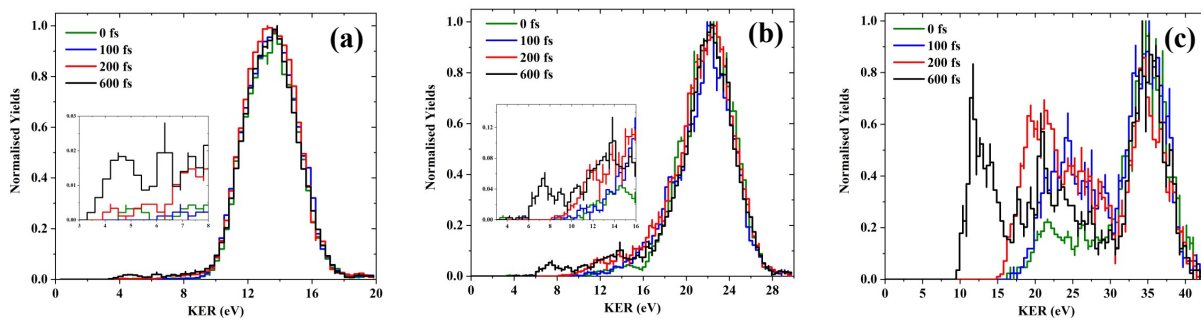


Figure 5.8: Kinetic energy release (KER) for three different three-body coincident channels after UV pump and NIR probe pulses at different delays. (a) $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$, (b) $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^+$, and (c) $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$. Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

5.1, for this charge state combination the (KER, Θ) map does not contain any pronounced contribution from the sequential fragmentation of long-lived metastable intermediates [72] and, thus, is well-suited for the search of potential photo-isomerization contribution [35] [34]. In the analysis below, we mainly focus on this channel, and use the lower charge states

mainly as complementary observables.

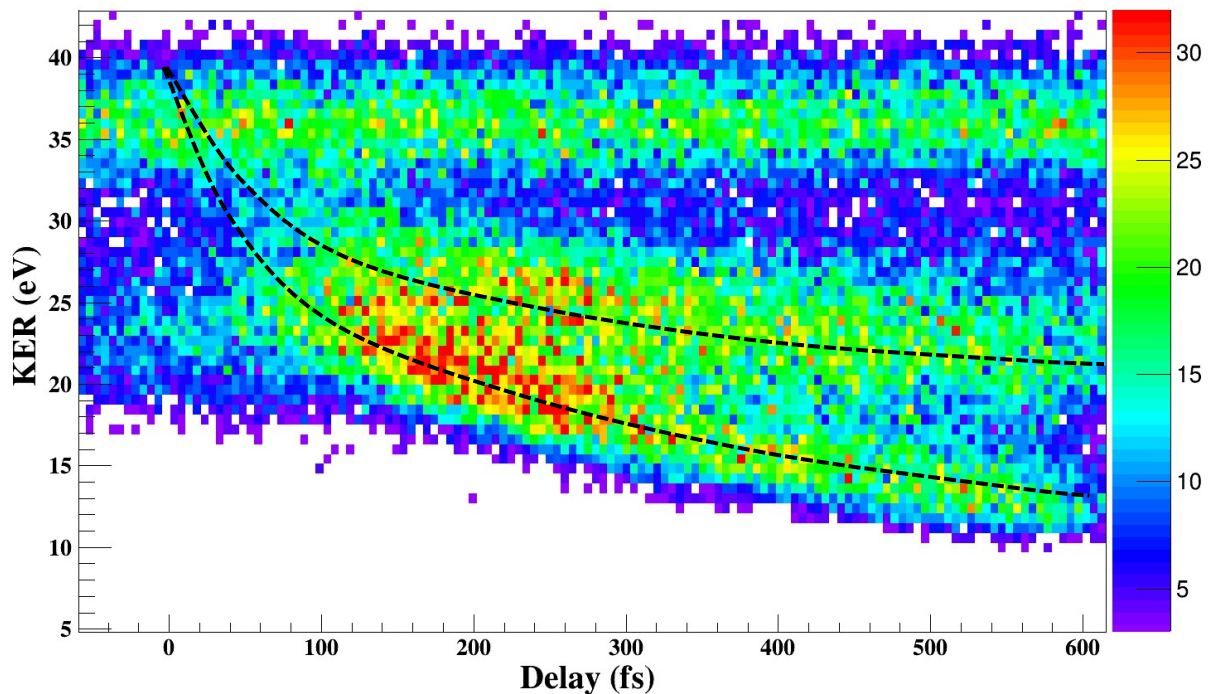


Figure 5.9: Delay-dependent kinetic energy release (KER) for the three-body coincident $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ channels after UV pump and NIR probe pulses. Dashed lines highlight the delay-dependent KER features. Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

Fig. 5.8 displays the 1D KER spectra measured for all three channels shown in Fig. 5.7 at four different delays. In each of these spectra, a variety of features propagating towards lower KER values with increasing delay can be observed. Noticeably, the pump-probe contrast, i.e., the ratio of delay-dependent to delay-independent features increases dramatically with increasing final charge state. The most likely reason for this is that the higher charge states results from the small central region of the NIR probe pulse focus, and, thus, samples the region of the highest photon fluence of the UV pump pulse, thus increasing the ratio of “pumped” to “un-pumped” (i.e., excited vs. unexcited) molecules. The same spectrum for the $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ channel is shown as a function of the delay in Fig. 5.9 (up to 650 fs). In this graph, besides relatively weak delay-independent band centered at 36 eV, two broad descending features (marked by black dashed lines) develop at larger delays. In general, these features can include $\text{CH}_2\text{I} + \text{I}$ (or $\text{CH}_2\text{I} + \text{I}^*$) dissociation channels discussed in the

previous section and, in addition, other possible pathways like three-body dissociation into $\text{CH}_2 + \text{I} + \text{I}$, or molecular iodine elimination, $\text{CH}_2^+ + \text{I}_2$. It should be noted that while potential three-body dissociation pathways are explicitly excluded in the two-body maps discussed above, the I_2 elimination pathways should be visible there. However, we did not find any clear delay-dependent signal in $\text{CH}_2^+ + \text{I}_2^+$ channel. Note that upon the absorption of a single UV photon, the energetic threshold for three-body dissociation was reported to be ~ 5 eV (corresponding to 248 nm) [44], and the fraction of I_2 elimination pathway compared to total reaction products at the same wavelength was reported to constitute less than 0.5% [51].

Fig. 5.10 depicts the evolution of (KER, Θ) maps in a broad delay range. In the left part of this figure (panels a-d), four graphs within the first 600 fs after the pump are shown. The right part (panels e-h) covers a range of much larger delays, reaching 20 ps in Fig. 5.10(h). The first map in Fig. 5.10(a), corresponding to the exact overlap of the pump and probe pulses, closely resembles a pattern obtained with single NIR pulse (see Fig. 4.11(c)), with two distinctly separated regions marked (1) and (2). This resemblance is not surprising since the UV pulse contributes very little to multiple ionization of a bound molecule, and the spectra in the overlap region are dominated by the effect of the NIR probe pulse. Noticeably, the circle marked (3) on the right from the main feature (1) is empty in Fig. 5.10 (a), with no contributions from long-lived metastable states characteristic to that area in the (KER, Θ) maps for lower charge states. A solid yellow circle in Fig. 5.10 (a), which reflects the prediction of the CE simulation for the isomerized $\text{CH}_2\text{I-I}$ geometry, falls exactly on the border between the regions marked (1) and (3).

After 100 fs, in Fig. 5.10 (b), area (2) starts to be filled with more events, reflecting the onset of different dissociation channels. Besides that, a noticeable numbers of events appear in region (3), and direct below it. In the next two frames in panels (c) and (d), the main part of the dissociating wave packet in the middle of each frame starts to visibly split in two. At the same time, the events disappear again from region (3), seemingly propagating downwards. At large delays (panels (e-h)), circle 3 is practically empty, regions (1) and (2) start to resemble their appearance at zero delays, and the two dissociating structures

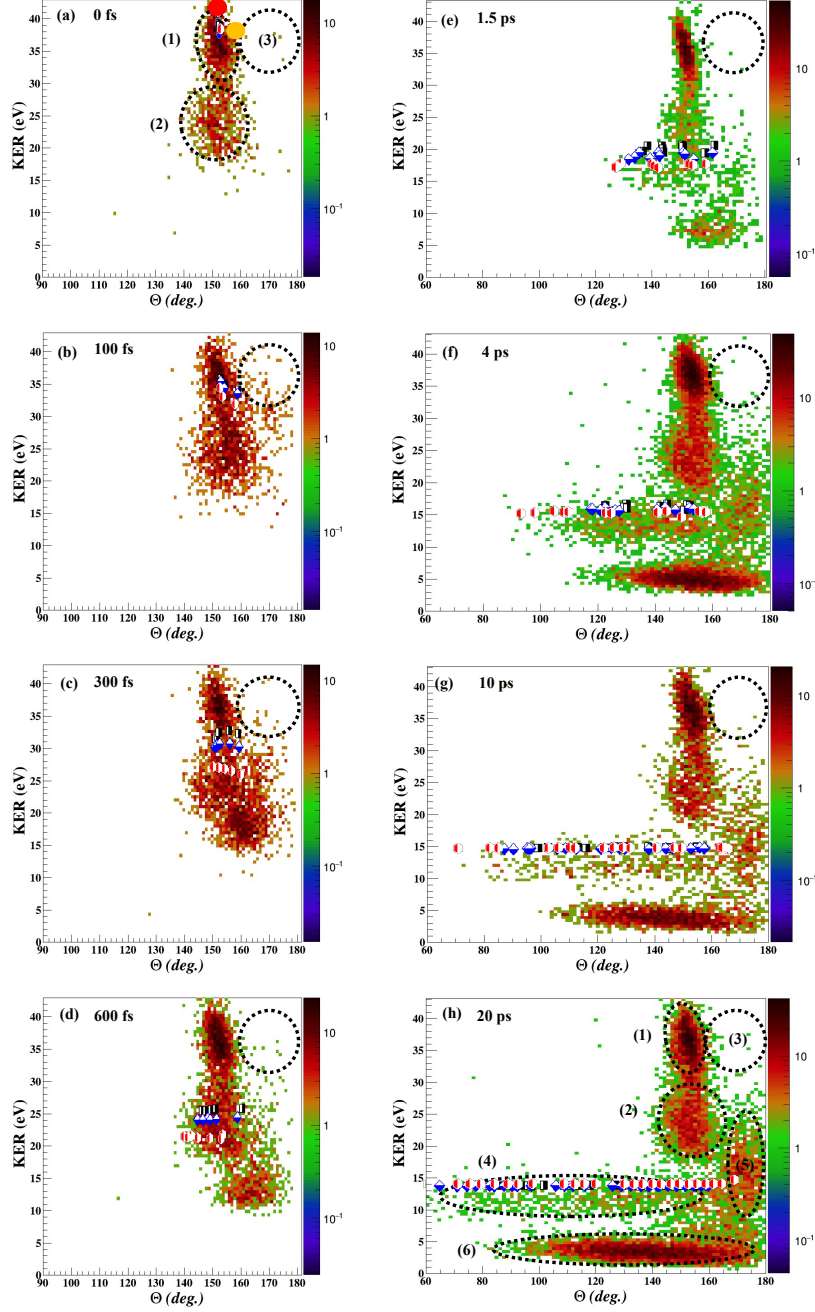


Figure 5.10: KER- Θ plots for the three-body $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ coincident channel at different delays: (a) 0 fs, (b) 100 fs, (c) 300 fs, (d) 600 fs, (e) 1.5 ps (f) 4 ps, (g) 10 ps and (h) 20 ps. Regions numbered (1) - (6) and marked by dashed lines indicate KER- Θ features corresponding to different pathways discussed in the text. In frame (a) at 0 fs, solid red circle depicts the simulated KER- Θ values for the instantaneous CE of the neutral CH_2I_2 molecule at its equilibrium geometry, whereas the solid yellow circle shows the results of the same simulation but starting with the isomerized $\text{CH}_2\text{I-I}$ geometry. Series of dots in different frames show the results of the CE simulation for the $\text{CH}_2\text{I} + \text{I}$ dissociation channel after the pump pulse, which takes into account the rotation of the CH_2I intermediate. Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

(marked (4) and (6) in panel (h)) are well separated, and are continuously extending to smaller angles. In parallel, a localized feature at 180° angle (marked (6)) becomes rather pronounced. In the following, we will analyze the events falling into each of 6 regions marked by the dotted lines in Fig. 5.10, and discuss their origin.

Delay-independent channels

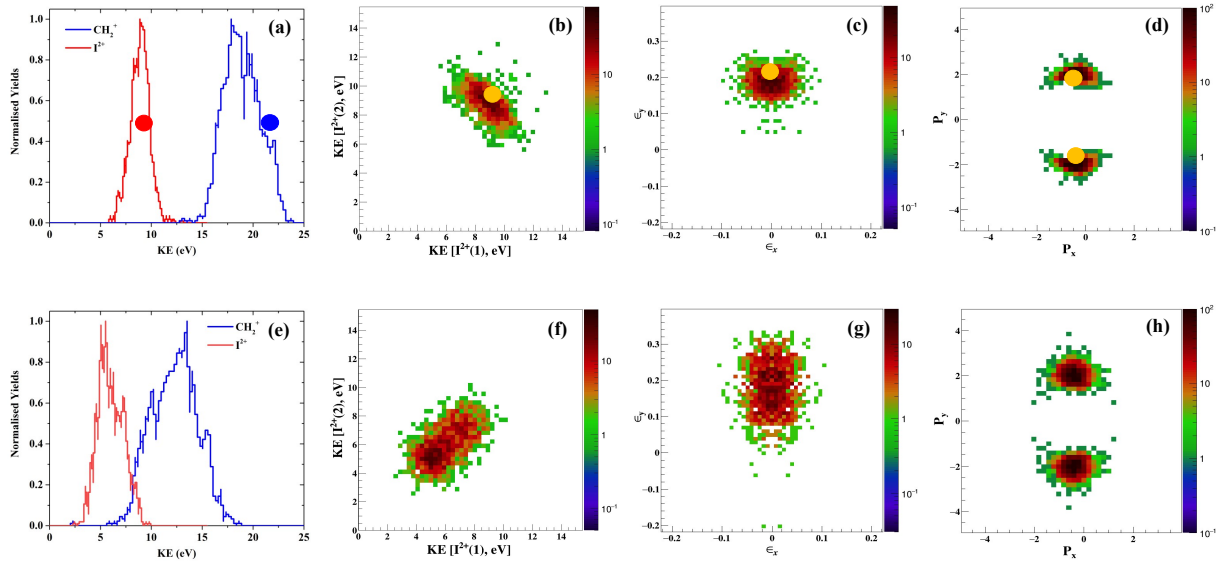


Figure 5.11: Different representations of the $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ coincident events in regions (1) and (2) of the KER- Θ plot at 0 fs. The plots in the upper row are for the region (1): (a) KE of coincident CH_2^+ and I^{2+} fragments, (b) KE sharing of I^{2+} fragments, (c) Dalitz Plot, and (d) Newton Plot. The lower row displays the same graphs but are for the region (2): (a) KE of coincident CH_2^+ and I^{2+} fragments, (b) KE sharing of I^{2+} fragments, (c) Dalitz Plot, and (d) Newton Plot. Solid circles in the upper row represent the simulated values for the instantaneous CE of the neutral CH_2I_2 molecule at its equilibrium geometry. Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

The structures visible in regions (1) and (2) appear very similar at zero delay, and above 4 ps, and closely resemble the results for a single NIR pulse shown in Fig. 4.10 (c). We therefore assign these two features to a CE of a bound molecule by the probe pulse alone. Region (1) to a large extent reflect our expectations for a concerted three-body breakup of a molecule. Even though the CE simulation falls into the upper border of the KER for this feature, as shown by the uppermost symbol in Fig. 5.10 (a), as discussed in sections 2.5 and

4.2 - 4.4, the KER overestimation by such a simple model for the case of bound molecule is very intuitive. Nevertheless, even such a simple model predicts reasonably well individual energies of the iodine ions shown in Fig. 5.11 (a), their energy sharing in Fig. 5.11 (b), as well as Dalitz and Newton plots in panels (c) and (d), respectively. There is noticeable spread of the events away from equal energy sharing (i.e., from the main diagonal in panels (b) and (f)).

The scenario behind the events in region (2) is less obvious. From the iodine energy sharing diagrams, Dalitz and Newton plots shown in Fig. 5.11 (e-h), we can clearly state that these events are generated via concerted fragmentation of the molecule. Interestingly, the energy sharing between the two iodines is even more symmetric than in the “main” feature in region (1), falling onto the diagonal in the energy sharing diagram in panel (f) and being localized on the central vertical line in the Dalitz plot in panel (g). The Newton plot in panel (h) is rather similar to that in panel (h). Although we do not know the exact mechanism responsible for this region, our preliminary analysis show that it could be populated via some of the dicationic configurations with significant bond elongation.

Both of these regions manifest exactly the same characteristic features at 10 ps, as detailed in Fig. 5.12. This proves that both of these regions are hardly influenced by the presence of the pump pulse, and originate from the CE of “intact” molecules, even though it needs to be stretched to enable smaller KER and individual KE of the fragments in region (2).

Transient photoisomerization of CH_2I_2

Next, we examine the origin of the events appearing in region 3 (marked by the dashed circle in the upper right corner in each of the panels of Fig. 5.10. This circle, which is nearly empty at zero delays, contains noticeable number of events at 100 fs, and loses them again, becoming nearly empty at 600 fs, is adjacent to the position, where we expect the events resulting from the the “linearized” isomer of diiodomethane, $\text{CH}_2\text{I-I}$ (see section 2.2, and Fig. 2.15 in section 2.5). The exact position predicted for an isomer CE is marked by the solid yellow symbol in Fig. 5.10 (a). Since it essentially falls onto the border of the

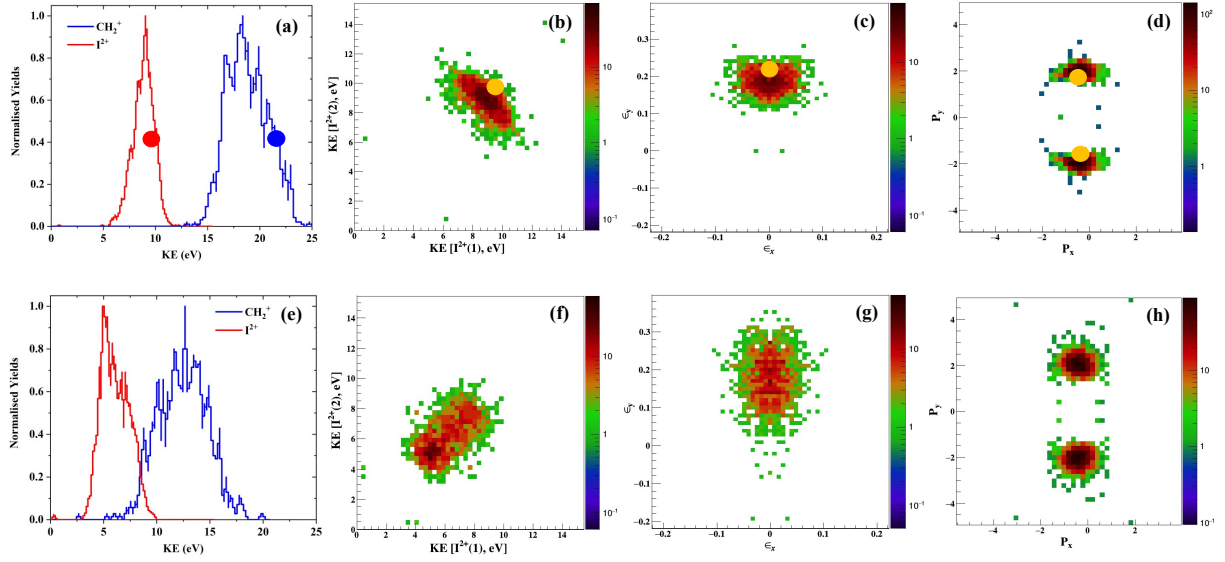


Figure 5.12: Different representations of the $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ coincident events in regions (1) and (2) of the KER- Θ plot at 10 ps. The plots in the upper row are for the region (1): (a) KE of coincident CH_2^+ and I^{2+} fragments, (b) KE sharing of I^{2+} fragments, (c) Dalitz Plot, and (d) Newton Plot. The lower row displays the same graphs but are for the region (2): (a) KE of coincident CH_2^+ and I^{2+} fragments, (b) KE sharing of I^{2+} fragments, (c) Dalitz Plot, and (d) Newton Plot. Solid circles in the upper row represent the simulated values for the instantaneous CE of the neutral CH_2I_2 molecule at its equilibrium geometry. Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

intense, delay-independent structure (1), which results from the CE of the “regular” CH_2I_2 configuration, we need further analysis to reveal potential signatures of isomerization. Our first consideration here is that we need to exclude dissociation events, and instead focus on the geometries resulting in large angles but, at the same time, large KER. According to the simulation, the CE of the isomer yields only $\sim 2 \text{ eV}$ lower KER than the “regular” geometry. This determined the choice of region 3, along with the appearance of transient events in that region. Another expectation for the isomerized geometry is a rather asymmetric iodine energy sharing.

Similar to Fig. 5.11 and 5.12, in Fig. 5.13 we plot individual particle KE, iodine energy sharing diagram, Dalitz and Newton plots for the events detected in region 3, at 80 fs delay between the pump and the probe pulses, which roughly corresponds to maximum signal within the circle (3). These patterns appear to be very different from those observed in Fig.

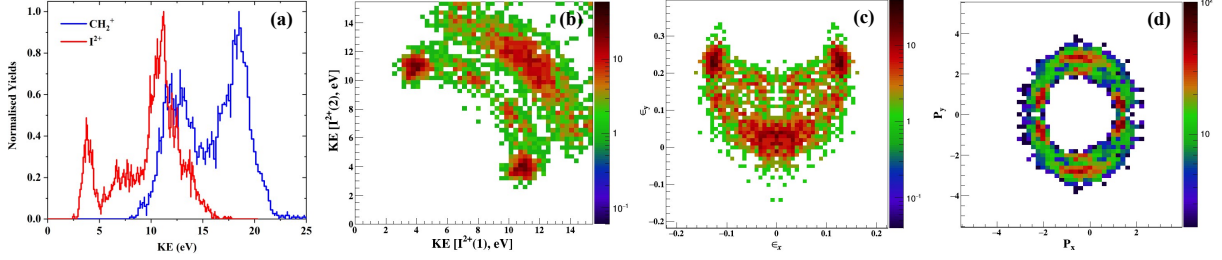


Figure 5.13: Different representations of the $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ coincident events in regions (3) of the KER- Θ plot at 80 fs: (a) KE of coincident CH_2^+ and I^{2+} fragments, (b) KE sharing of I^{2+} fragments, (c) Dalitz Plot, and (d) Newton Plot. Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

5.11 and 5.12 for regions 1 and 2, with a significant number of events displaying unequal energy sharing between the two iodine ions, as can be clearly seen in Fig. 5.13 (b,c). However, the spectra seem to manifest at least two different features, with two clear peaks in CH_2^+ KE distribution in panel (a), and two distinctly separated islands in energy sharing diagram (b) and Dalitz plot (c).

To reveal the nature of rather complex three-particle CE patterns for region 3 observed in Fig. 5.13, we follow the same logic we used to elucidate I_2/I_2^+ formation in section 4.4. We start with examining the sum KE of the two iodines, as well as CH_2^+ KE for dissociating and non-dissociating events. As can be seen in Fig. 5.9 and 5.10, in the five-fold charge states we are considering here, we can coarsely separate those by the KER value falling above or below 32 eV. In Fig. 5.14, we plot the sum KE of two I_2^+ ions (panels a, b) and CH_2^+ KE (panels c and d) for the KER values above (a, c) and below (b, d) 32 eV. Several interesting observations can be made inspecting these plots. First, the dissociating part seem to be quite different from what we observed in the previous Chapter using NIR pump pulses (see Fig. 4.29, 4.30, 4.49). Instead of two very distinct lines in the delay-dependent distribution of the sum KE of two halogens (one horizontal and one descending), here, we observe a broad feature propagating downwards, and some diffuse structure with the sum KE values growing as a function of the delay. Second, more important, even the spectra for $\text{KER} > 32 \text{ eV}$, seem to contain some noticeable dynamics. Specifically, there is a weak but noticeable descending band in CH_2^+ energy. In addition, some events result in increase of (I, I) sum KE, and there

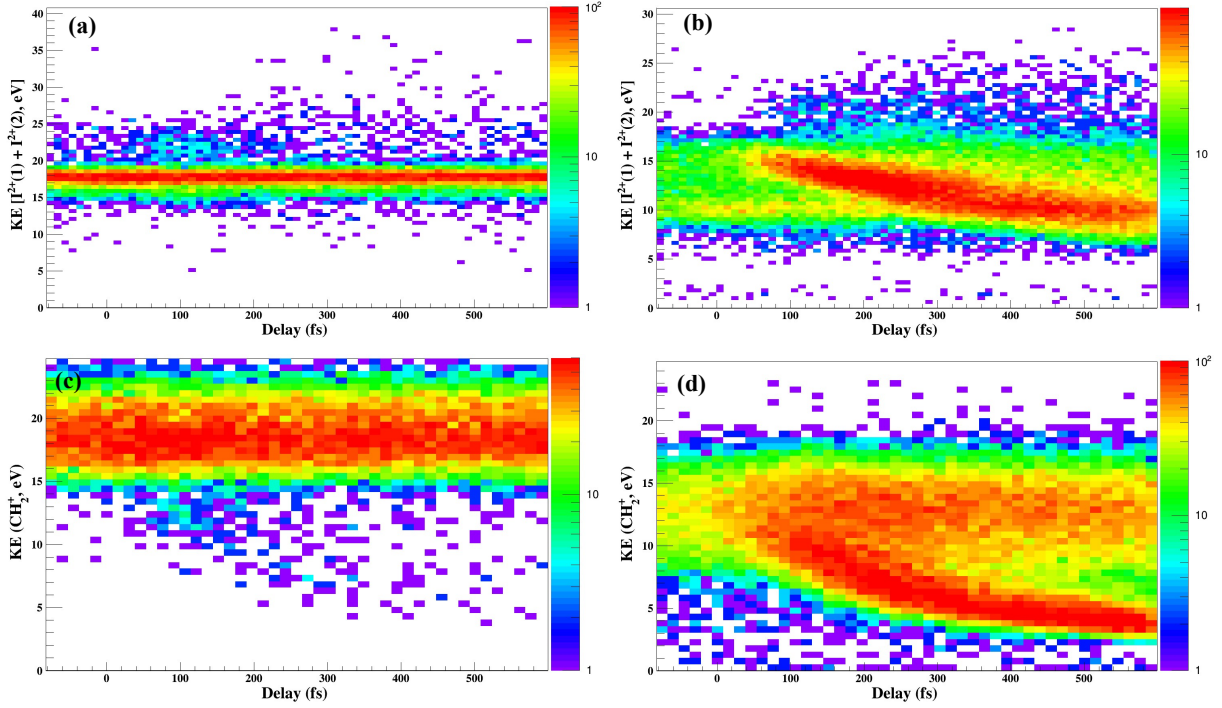


Figure 5.14: Delay-dependent kinetic energy (KE) of three-body coincident CH_2^+ and I_2^+ fragments for different KER conditions. In the upper row, delay-dependent sum KE of I_2^+ fragments is plotted for $\text{KER} > 32$ eV (a) and $\text{KER} < 32$ eV (b). Similarly, in the lower row, delay-dependent KE of CH_2^+ fragments is plotted for $\text{KER} > 32$ eV (c) and $\text{KER} < 32$ eV (d). Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13}$ W/cm² while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14}$ W/cm².

is a localized structure just above the main band at ~ 100 fs. Since there seem to be some dissociation pathway creating the CH_2^+ ions with decreasing KE, we now examine the CH_2^+ ion KE distribution for the events falling within circle (3), which is plotted in Fig. 5.15 as a function of UV-NIR delay. Here, we indeed observe a broad, diffuse band propagating towards lower KE with increasing delay. At 80 fs delay, it can be coarsely separated from the delay-independent band by the dashed line marking the CH_2^+ KE of 15 eV.

As a next step, in Fig. 5.16 we plot the three-particle coincident patterns for region (3), which we already considered in Fig. 5.13, but now with the condition on the CH_2^+ KE lying above 15 eV (panels a-c) and below 15 eV (panels d-f). The latter condition clearly separates events with symmetric iodine energy sharing, which cannot result from the isomerized geometry. In contrast, the spectra with the CH_2^+ KE > 15 eV in the upper row, exhibit rather unequal energy sharing. Comparing the results in these graphs with

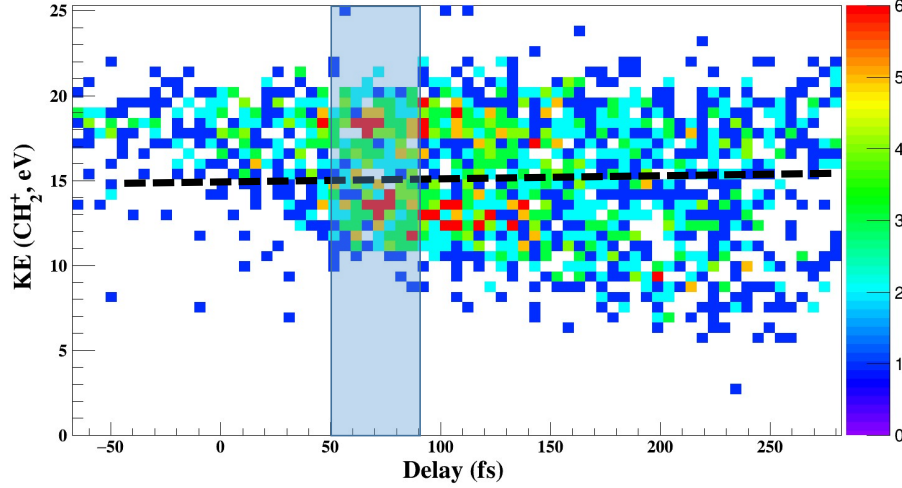


Figure 5.15: Delay-dependent KE of the CH_2^+ fragments from the $\text{CH}_2^+ + \text{I}_2^+ + \text{I}_2^+$ channel in region (3) of the KER- Θ plot. Dashed line separates the KE region < 15 eV and > 15 eV. Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13}$ W/cm 2 while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14}$ W/cm 2 .

the simulation for the CE of the isomer, we conclude that these events most likely reflect the photoisomerization of CH_2I_2 . In contrast, the decreasing CH_2^+ KE and the symmetric emission of the two iodines with rather large KE in the graphs shown in the lower row suggests that those events result from the detachment of CH_2 and “synchronous” I_2 formation.

As can be seen in Fig. 5.10, the whole population in region (3) is gone again at 600 fs. In order to trace the time scale for the isomerization process, in Fig. 5.17, we plot the yield of the events in region (3) as a function of pump-probe delay, with the condition that the CH_2^+ KE is larger than 15 eV (corresponding to the upper row in Fig. 5.16). The yield curve exhibit a pronounced maximum ~ 80 to 100 fs. By fitting this delay-dependent yield with the exponential grow and decay curves, we found the rise time of this channel to be 74 ± 16 fs, and the decay time – 116 ± 10 fs.

$\text{CH}_2\text{I} + \text{I}$ channel and CH_2I rotation

Besides delay-independent features (1) and (2) and weak transient contribution that appears in region (3), three major delay-dependent features can be observed in the KER vs. angle maps shown in Fig. 5.10, which become clearly distinguishable at large delays, and are

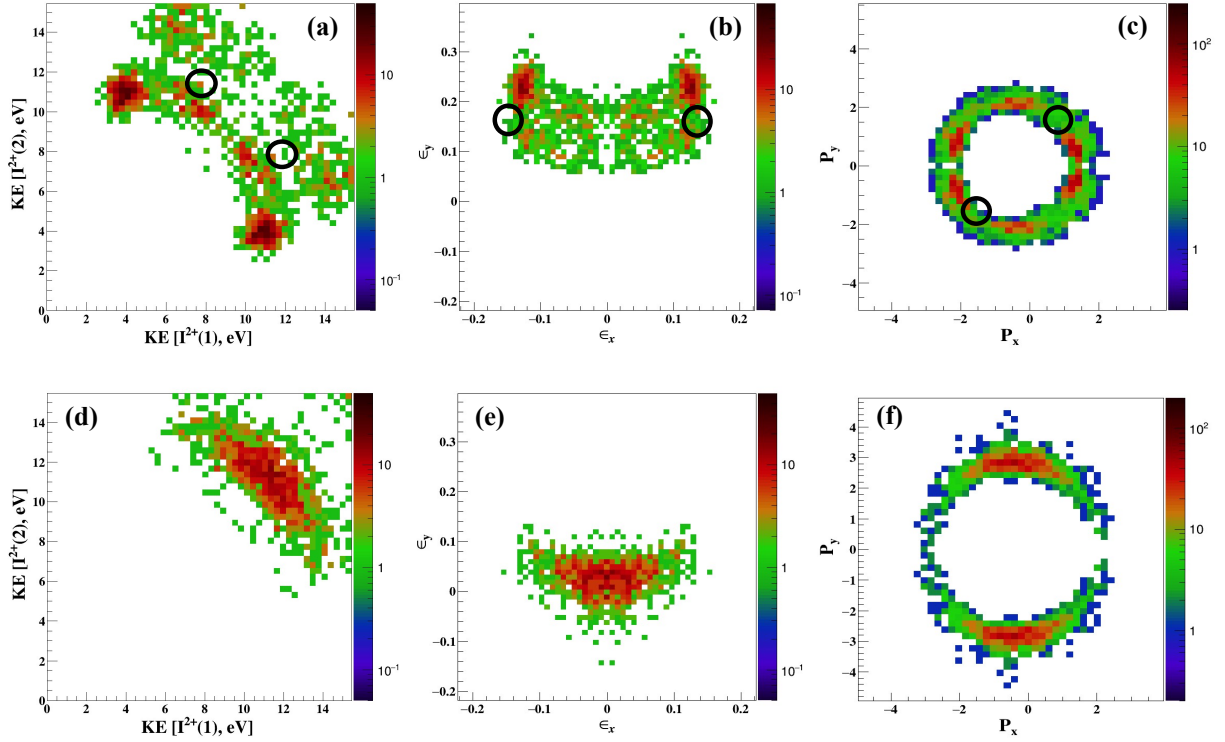


Figure 5.16: Different representations of the $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ coincident events in regions (3) of the KER- Θ plot at 80 fs for different KE values of the CH_2 fragment. Upper row: CH_2^+ KE > 15 eV. (a) KE sharing of I^{2+} fragments, (b) Dalitz Plot, and (c) Newton Plot. Lower row: CH_2^+ KE < 15 eV. (d) KE sharing of I^{2+} fragments, (e) Dalitz Plot, and (f) Newton Plot. Open circles represent the simulated values for the instantaneous CE of the neutral molecule starting from the isomerised $\text{CH}_2\text{I-I}$ geometry. Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

marked (4), (5) and (6). We first consider band (4), which appears as a structure broad in angle in the KER range between 10 and 15 eV. This band reflects a dominant dissociation pathway $\text{CH}_2\text{I} + \text{I}$ (or $\text{CH}_2\text{I} + \text{I}^*$), which we discussed in the previous section as a dominant feature in two-body breakup patterns. In three-body CE final state, this channel ends up at large delays with rather high KER, determined asymptotically by the CE of the CH_2I molecular fragment. Correspondingly, one expects that most of the energy is taken by the CH_2^+ ion, and that of the two iodines that remained bound to CH_2 at the time of the probe pulse arrival, one acquires higher energy than the other. This is exactly what we observe for the events from the region (4) in Fig. 5.18, where the individual fragment KE distributions (a), (I, I) energy sharing (b), Dalitz (c) and Newton (d) plots are shown for region(4) at 10

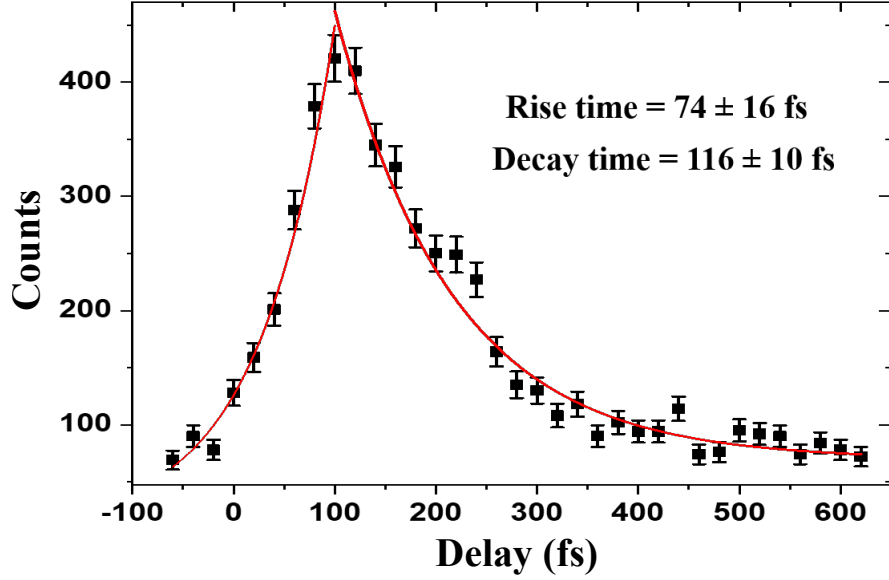


Figure 5.17: Yield of the three-body events in region (3) as a function of UV-NIR delay.

ps delay. As can be seen in panels (a-c), the main portion of energy is taken by CH_2^+ , and while both iodines have rather low KE, they share it unequally, with one of them almost always at nearly zero KE (panel (b) in Fig. 5.18).

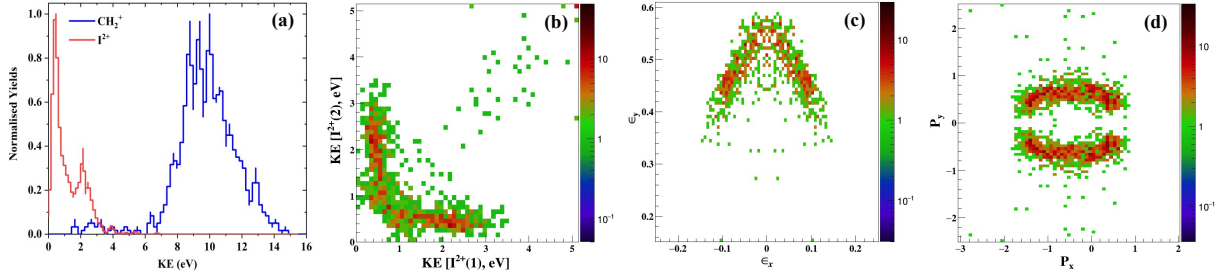


Figure 5.18: Different representations of the $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ coincident events in regions (4) of the KER- Θ plot at 10 ps: (a) KE of coincident CH_2^+ and I^{2+} fragments, (b) KE sharing of I^{2+} fragments, (c) Dalitz Plot, and (d) Newton Plot. Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

While in this scenario one of the iodine ions is always emitted opposite to the CH_2^+ ions, which is consistent with the Newton plot shown in Fig. 5.18 (d), the overall angular structure of the Newton plot appears to be rather broad. This is consistent with a very broad angular distribution feature (4) shown at large delays in Fig. 5.10. This broad distribution mainly originates from rotation of the intermediate CH_2I fragment. As discussed

in Section 2.2, the breakage of one of the CI bonds exerts a significant torque on the molecule because the initial direction of force does not coincide with the line connecting the centers of mass of the fragments [98] [86]. Accordingly, a major fraction of the excess energy upon photoabsorption is taken by the internal degrees of freedom (rotation), while, as shown in the previous section, only $\sim 20\%$ of this excess energy appears as a translational energy of the fragments. Signatures of CH_2I rotation were directly observed in a recent UED experiment [50]. In order to verify the role of this rotation, we have added rotation with 370 fs period determined in [50] to our CE simulation. The result of the modified simulation is shown in Fig. 5.10 as a series of dots at each delay. Because of the finite time resolution of the experiment and the presence of different velocities in the wave packet, we have included the results for several translational energies (as in section 5.3) and, at each point covered a certain range of delays centered at the value shown in the corresponding panel of Fig. 5.10. It can be seen from these data that the simulations described the evolution of the broadening angular distribution of the CE events very well. It still overestimates the KER value, because even at large delays, we deal with the CE of a bound CH_2I fragment, and, as discussed throughout this thesis, the CE simulation normally overestimates the KE for bound molecules.

Molecular I_2 elimination

While the fragmentation of CH_2I_2 into $\text{CH}_2 + \text{I}_2$ channel (with one of the fragments being neutral, and another – ionic) was a major feature in our NIR-NIR pump-probe results, we did not find a clear signature of this channel being triggered by the UV pump in our two-body CE analysis presented in the previous section. Nevertheless, we observe clear signatures of this channel in our three-body CE patterns. To demonstrate this, we start with the procedure we developed in the previous Chapter for NIR-NIR experiments, namely, selecting the events where the sum KE of the two halogen atoms is rather high. As can be seen in Fig. 5.14 (b), in the present UV-NIR data the separation between the two channels in sum KE of the two iodines from dissociating molecules is not as clear as in NIR-NIR case (compare Fig. 5.14

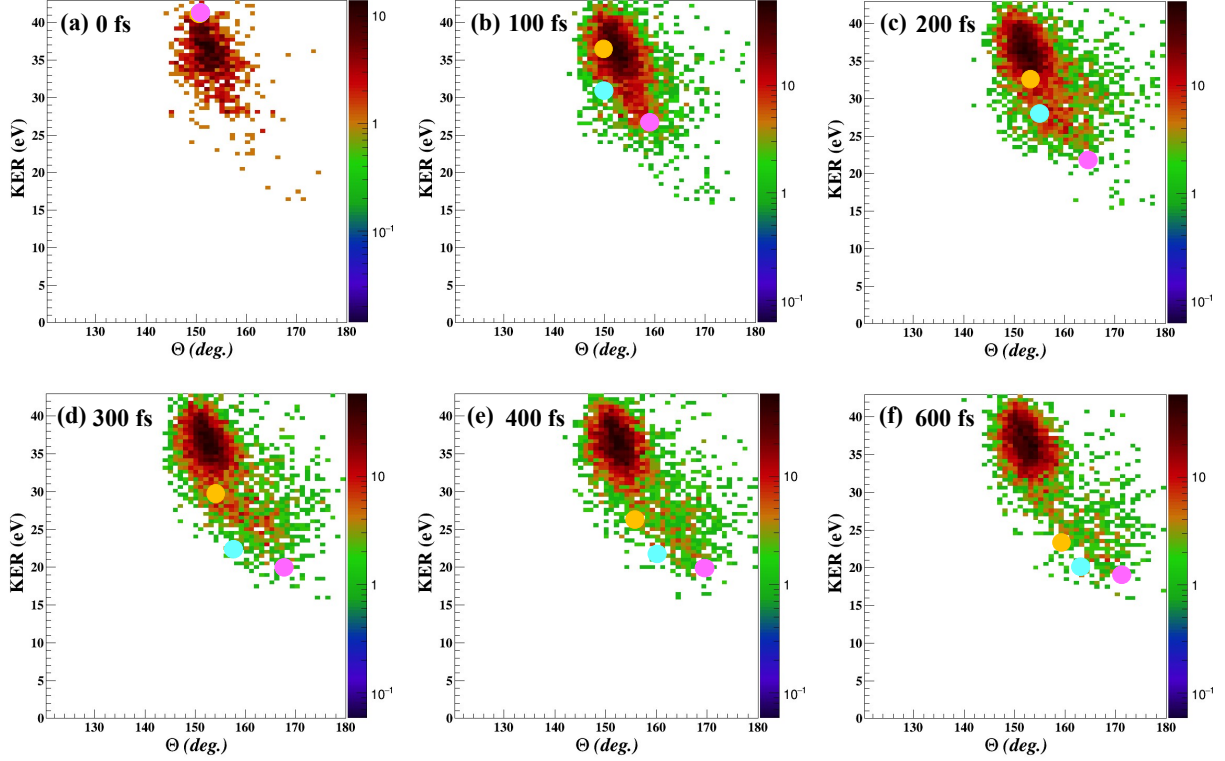


Figure 5.19: KER- Θ snapshots at different delays for the condition $\text{sum KE (I}^{2+} + \text{I}^{2+}) > 15 \text{ eV}$. (a) 0 fs, (b) 100 fs, (c) 200 fs, (d) 300 fs, (e) 400 fs and (f) 600 fs. Solids circles represent the results of the CE simulation for the $\text{CH}_2 + \text{I}_2$ fragmentation channel after the pump pulse assuming different asymptotic dissociation energies: pink = 0.8 eV, cyan = 0.25 eV and yellow = 0.15 eV. Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

(b) and 4.29 (b)). Nevertheless, by gating on the sum KE of the iodines above 15 eV, we can clearly select the events outside of the descending band. In fact, as can be seen from Fig. 5.14, in this case some of the events exhibit larger (I, I) sum energy than the bound molecule. In Fig. 5.19 we present a series of (KER, Θ) snapshots obtained at different delays with the condition that the sum KE of the two iodines is above 15 eV. Note that this condition filtered out structure (2) at zero delays present in all previous (KER, Θ) plots. Besides the delay-independent feature (1), these snapshots contain two important structures. First, we see a band descending to smaller KERs and large angles, pretty similar to what we observed in NIR-NIR pump probe experiments. We believe that this feature reflects direct I_2 elimination pathway. The symbols shown in each panel depict the predictions of the CE simulation (assuming two different translational energies), which fit the data in this region

reasonably well.

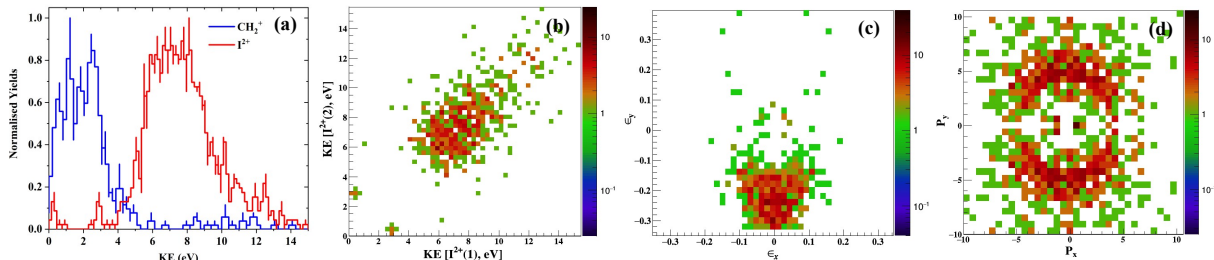


Figure 5.20: Different representations of the $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$ coincident events in regions (5) of the KER- Θ plot at 10 ps: (a) KE of coincident CH_2^+ and I^{2+} fragments, (b) KE sharing of I^{2+} fragments, (c) Dalitz Plot, and (d) Newton Plot. Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

In addition, there is a group of events, clearly visible in 100 fs and 200 fs frames, which appear with rather large KER at large angles, “passing” through the region (3) discussed above. In our analysis of the isomerization process, we have seen that some of the events in this region do manifest small CH_2^+ KE, large KE of both I^{2+} , their symmetric emission angles and equal energy sharing (see the lower row of Fig. 5.16), characteristic for direct I_2 elimination. Moreover, one would expect that the isomerized molecules decay, at least partially, via I_2 ejection.

As can be seen in the right panels of Fig. 5.10, at larger delays the two features discussed above merge, and end up as a feature marked (5), at nearly 180 degree between the two iodine momenta in Fig. 5.10 (h). From this graph, it becomes clear that the selection of events with sum (I, I) KE above 15 eV is rather arbitrary, and cuts a substantial fraction of events from this group. In Fig. 5.20, we show our “standard” set of three-body observables for this region (5) at 10 ps delay. These graphs highlight all the features of I_2 elimination channel discussed above which become even more pronounced at this large delay. In this case the CH_2 fragment detached by the pump carries nearly zero energies, whereas both iodines that are stack together, still receive massive CE energy, and are emitted back to back.

Besides the events marked in region (5), there is also a contribution spreading out of this area towards lower KERs. It exhibits most of the features typical for I_2 elimination (in particular, preferential back to back emission of two iodines and low fraction of energy

taken by CH_2^+), but with the iodine energies also moving to lower values with increasing delays. Similar to what we discussed in relation to Fig. 4.32 (d), we assume that these events result from the creation of metastable molecular iodine, which decays on a ps time scale comparable with our delay range.

Three-body dissociation

Besides dissociation, isomerization and I_2 elimination channels discussed above, there is an additional feature (marked (6) in Fig. 5.10), which is not compatible with any of the above scenarios. It appears at small delays as a group of events propagating towards low KERs rather early, and becomes clearly separated from the other features starting from ~ 600 fs delays (Fig. 5.10 (d)). In contrast to $\text{CH}_2\text{I} + \text{I}$ dissociation channel, the events in this group continue moving to even lower KERs at larger delays, falling below 5 eV at 20 ps. They also spread in (I, I) emission angle. Although not as strongly as $\text{CH}_2\text{I} + \text{I}$ channel in region (4).

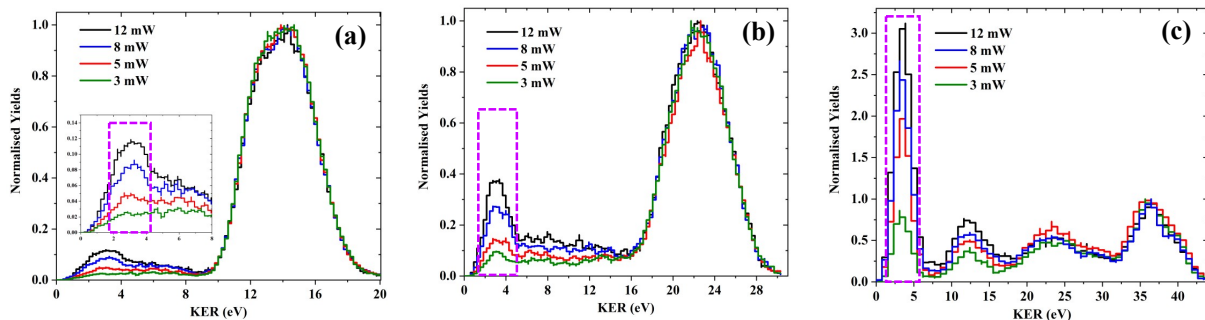


Figure 5.21: KER distribution for three-body coincident channels in different final charge states at different UV powers: (a) $\text{CH}_2^+ + \text{I}^+ + \text{I}^+$, (b) $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^+$ and (c) $\text{CH}_2^+ + \text{I}^{2+} + \text{I}^{2+}$. Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

The only scenario compatible with the above observations is a three-body dissociation into CH_2 and two iodines (all either neutral or charged) triggered by the pump pulse. Then, at large delays, the Coulomb repulsion becomes negligible, and the measured KER converges towards dissociation energy. If any of the three fragments we observe in the final state would be bound to another one at the time when the probe pulse arrives, the CE energy in five-fold charge state we consider here would be much larger than the values observed for structure

(6). This assignment is supported by the results presented in Fig. 5.21, where the angle-integrated KER distributions measured at 10 ps delay for three different three-body final states are shown. The low-energy feature discussed above appears in all three graphs, and does not depend on the charge state. This provides another evidence that the Coulomb repulsion becomes negligible, which means that all three partners are far away from each other at the time when the probe pulse arrives. In this figure, the measured KER spectrum is also shown for several different UV pump pulse powers. The low-energy feature manifests a pronounced dependence of the UV-power, which will be discussed in the next section.

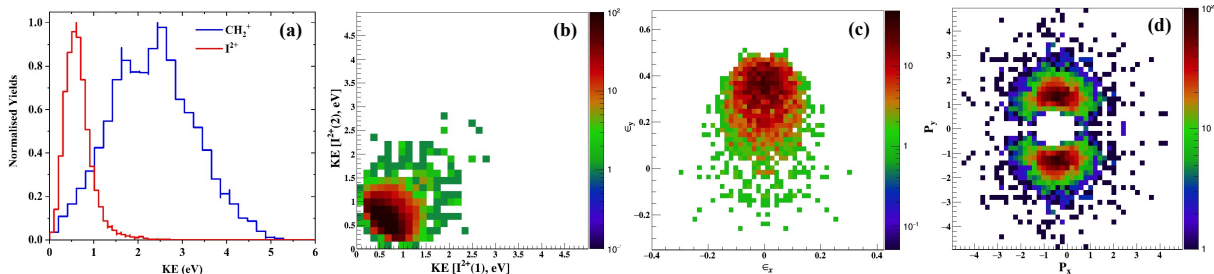


Figure 5.22: Different representations of the $\text{CH}_2^+ + \text{I}_2^+ + \text{I}_2^+$ coincident events in regions (6) of the KER- Θ plot at 10 ps: (a) KE of coincident CH_2^+ and I_2^+ fragments, (b) KE sharing of I_2^+ fragments, (c) Dalitz Plot, and (d) Newton Plot. Intensity of UV pump pulse is kept $\sim 2.4 \times 10^{13} \text{ W/cm}^2$ while the intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

Fig. 5.22 presents the same “standard” set of three-body observables as Figs. 5.11-5.13, 5.16, 5.17 and 5.20 for the events in Region (6) measured at 10 ps. This is fully consistent with the suggested scenario of three-body dissociation by the pump. Interestingly, despite rather broad spread in (I, I) angle observed in Fig. 5.10 for this channel, the Newton diagram in Fig. 5.22 (d) shows distinct angular correlation between the fragments, indicating that the initial three-body fragmentation is most likely concerted. The spread in (I, I) angles then likely results from the distribution of initial conditions for dissociation.

5.5 Summary and discussion

In the analysis presented above, we identified signatures of four basic photochemical processes in UV-irradiated diiodomethane: (1) dissociation of one C-I bond; (2) transient photoisomer-

ization into $\text{CH}_2\text{I-I}$ geometry and its subsequent decay; (3) molecular I_2 elimination; and (4) three-body dissociation. All these processes have been identified in terms of nuclear motion involved, with no direct information on the electronic states on which these dynamics unfold. For channel (1), $\text{CH}_2\text{I} + \text{I}$ dissociation, the pathways for this reaction are well-known from literature, and our findings are fully consistent with the previous knowledge on one-photon triggered dynamics. We also visualized the role of intermediate fragment rotation for this process. While the isomerization reaction (2) is also energetically accessible upon single-photon absorption, the information on this channel in literature is too scarce, especially in a gas phase, such that besides the sub-100 fs time scale, it is difficult to directly compare our results with previous work [35] [36].

In contrast to the first two channels, the probability of I_2 elimination (channel 3) upon the absorption of a single UV photon was reported to be very low [51], and the threshold for three-body dissociation is assumed to be higher than our photon energy [44]. However, it is not surprising that these channels are present in our data since our UV intensities allow for two- or three-photon transitions as well.

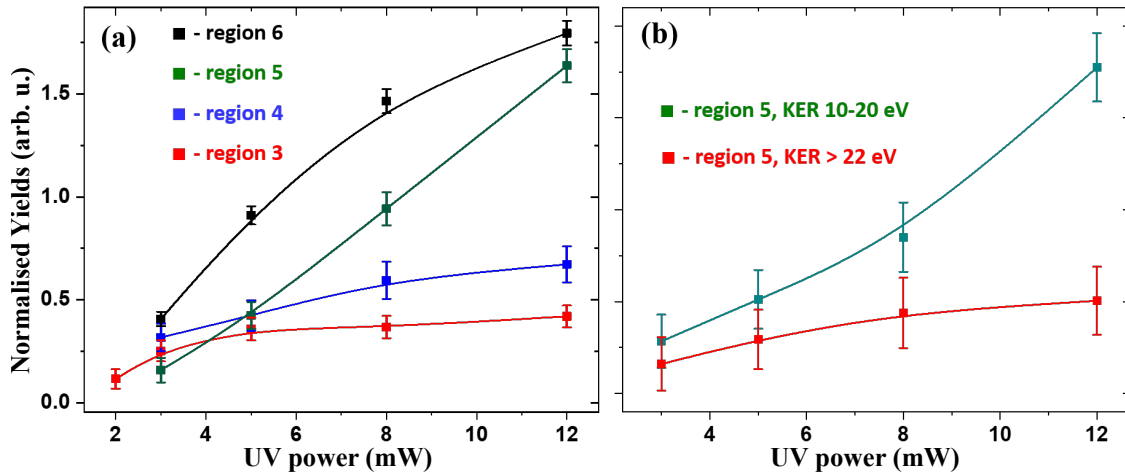


Figure 5.23: UV power dependence of the yield of coincident $\text{CH}_2^+ + \text{I}_2^+ + \text{I}_2^+$ channel in different regions of the KER- Θ plot: (a) Total yields in region (3-6). (b) Yields in region (5) for different KER values. The data for regions (4-6) are taken at 10 ps UV-NIR delay, whereas the yields for region (3) are measured at 80 fs delay, where it approaches its maximum value. The power of 12 mW corresponds to the UV intensity of $\sim 2.4 \times 10^{13} \text{ W/cm}^2$. The intensity of NIR probe pulse is kept at $\sim 5 \times 10^{14} \text{ W/cm}^2$.

To evaluate the role of such higher-order transitions, in Fig. 5.23 (a), we present the yields of the four channels discussed above measured as a function of the UV pulse power. The regions labeled in this figure refer to the areas in (KER, Θ) maps marked in Fig. 5.10. While for the isomerization channel this UV power scan was performed at 80 fs delay, for all other channels it was carried out at 10 ps, where all these channels are well separated. Two groups of curves exhibiting clearly different behavior are visible in this graph. The curves for CH₂I+I channel (region 4, blue) and for isomerization pathway (region 3, red) initially grow linear with UV power, and quickly saturate around 4-5 mW UV power. In contrast, the curves for I₂ elimination (region 5, green) and for three-body dissociation (region 6, black) display a steeper slope, with the fits yielding the power of ~ 1.3 -1.5 for UV power dependence). We interpret this as a confirmation of our initial assignments: while the C-I bond breaking and isomerization pathways are dominated by a single-photon absorption, the three-body dissociation and I₂ elimination channels are largely driven by the two-photon (or even higher order) processes.

Even though all the slopes of the power-dependent yield curves are influenced by the saturation of the first absorption step (which, according to the absorption cross section and laser focusing parameters is expected at ~ 4 -5 mW), the non-integer powers obtained from the fits are likely an indication that competing reaction pathways might be involved. In certain cases, they can be further disentangled based on the experimental data. An illustration of this is given in Fig. 5.23 (b), where the events in region 5 (corresponding to I₂ formation) are further sub-divided in their KER values. While the curve for 10-20 eV KER region exhibits even steeper slope than the green curve for the whole region in Fig 5.23 (a), the red curve reflecting the high-KER tail closely resembles the behavior observed for isomerization or C-I bond dissociation channels. The most likely scenario behind this difference is that the direct I₂ elimination, which results in the KERs below 20-22 eV, is very weak upon single photon absorption, and the signal we observe in that area results from the two-photon process via one of the Rydberg states, or even via ionic channels involving a three-photon pathway. In contrast, the events at 180 degree with higher KERs likely result from the decay of the isomer, which is one-photon driven.

Chapter 6

Dissociative ionization and electron transfer in iodomethane and chloriodomethane studied in XUV pump – XUV probe experiments

6.1 Motivation and schematics for XUV pump-probe experiments on valence shells

After considering molecular dynamics triggered by UV photons or by intense NIR pulses in two previous Chapters, here we will discuss the dynamics triggered and probed by the absorption of a single XUV photon. Our background motivation for this study has been outlined in section 2.4. The main objective of this work is to exploit the knowledge and imaging know-hows we developed in the analysis of strong-field induced cationic dynamics to characterize the dissociation of ionic states after XUV ionization of halomethanes, and to exploit this knowledge to study electron transfer (ET) in dissociating molecules beyond the validity of the classical over-the-barrier (COB) model.

Here, we use one XUV photon to ionize a molecule and launch a dissociating nuclear wave packet, which is characterized by Coulomb explosion (CE) imaging after the ionization of a second electron by the delayed replica of the same XUV pulse. This characterization allows us to assign a particular internuclear separation to a given pump-probe delay for major dissociation channels. Then we focus on doubly-ionized final states with asymmetric charge distributions resulting in one neutral and one doubly charged fragment. Similar to inner shell experiments [74] [76] [77] [78], [80] [52] [81] briefly discussed in section 2.5, we rely on the detection of low-energy doubly charged ions to monitor the production of a neutral partner as a function of pump-probe delay and, thus, as a function of internuclear distance. A major difference to these inner-shell experiments is that a hole which gets filled via distance-dependent ET is created by valence photoionization. Thus, instead of relying on a local nature of inner-shell absorption process, we select the events resulting from the absorption on a particular site by considering the events that most likely result from a particular “precursor” dissociating channel.

For this study, we have chosen iodomethane (CH_3I) and chloriodomethane (CH_2ICl) molecules as targets. The use of CH_3I allows for a direct comparison with numerous earlier experiments, whereas in CH_2ICl we can exploit double ionization at either molecular site upon halogen atom (or ion) detachment, which does not work with the methyl group in CH_3I . For this study, we have chosen the wavelength of ~ 53 nm (23.4 eV), which is slightly below the double ionization threshold for both systems, and also below the ionization limit of He, which was used as a carrier gas for CH_2ICl experiment. At this photon energy, the ionization is rather orbital insensitive. All of the molecular orbitals with ionization potential less than the photon energy can be ionized with comparable cross-section. For example, as shown in Ref. [92], the ionization cross-sections of the three most intense bands of CH_3I at about 23 eV are 35% ($\tilde{X}$), 18% ($\tilde{A}$), and 45% ($\tilde{B}$), where ($\tilde{A}$) state results in the dissociation limit of $\text{CH}_3 + \text{I}^+$.

The concept of this experiment is detailed in Fig. 6.1 for the example of CH_2ICl . The molecule is first ionized by a single 53 nm photon, creating a “precursor” dissociative state and then further ionized by another XUV photon with the same energy at different internu-

clear distances. Different from the previous inner-shell studies, where ET is always observed from light to heavy element, here we can also observe an additional ET channel where the ET happens from the heavy element to light moiety in the dissociation of CH_2ICl , i.e. $\text{I} \rightarrow \text{CH}_2\text{ClI}^{2+}$. At short internuclear distances, the overlap between wave functions of the two sites forming a molecular orbital through which the charges are quickly redistributed over the whole molecular system. In this case, the molecule will dissociate into two singly charged ions by the Coulomb explosion (CE). At internuclear distance longer than the critical distance R_c , ET is forbidden due to the increasing potential energy barrier between two sites. The height of the potential energy barrier is calculated by the COB model briefly outlined in section 2.4, which was in excellent agreement with the inner-shell x-ray probe experiments [87] [74] [76]. As shown in Fig. 6.1, the solid curves and the dashed lines present the potential energy barrier by the COB model and the ionization potential of the neutral moiety in presence of the Coulomb field of the dicationic co-fragment..

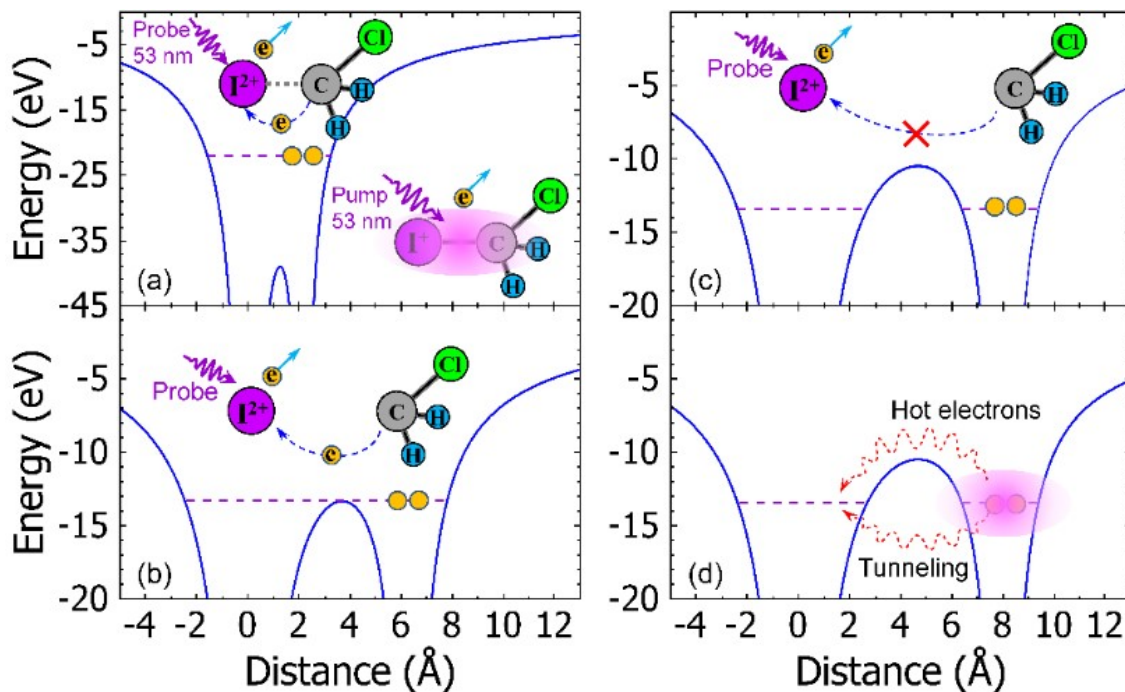


Figure 6.1: The pump-probe concept and classical over-the-barrier model. (a), (b), and (c) show the potential energy barrier of the internuclear distance within, equal to, and outside the critical distance. (d) shows the concept of tunneling effect and thermal energy induced electron transfer beyond the COB model.

In these experiment, we observe a pronounced ET outside the critical distance which deviates from the predictions from COB model. To address this issue, two mechanisms beyond the COB model are considered, as shown in Fig. 6.1 (d). On one hand, we find that the tunneling effect slightly improves the description. On the other hand, the thermal energy of the electron provides an opportunity to overcome the potential barrier. In order to better quantify our findings, we employ a semi-classical model developed by Enliang Wang, which is based on the reaction rate equation of the ET. A reasonable agreement between the semi-classical model and the experiment is achieved at a long distance.

6.2 Experimental details

The experiment was carried out using the ion part of the reaction microscope (ReMi) spectrometer installed at the free-electron laser FLASH2 in Hamburg [110], as described in section ???. In brief, the unfocused FEL beam passed through the main chamber and was split into two replicas, back-reflected and focused into a supersonic gas jet by a slit-mirror arrangement. To produce a gas-phase molecular target, helium was used as a seeding gas. The gas mixture was expanded through a 30 μm diameter nozzle and then collimated by two skimmers with 180 and 400 μm , respectively. The charged fragments were accelerated by a homogeneous electric field of 40 V cm⁻¹ towards a temporal- and position-sensitive detector. The three-dimensional momentum vectors of the ionic fragments were reconstructed from the measured time-of-flights and hit positions on the detector.

During the measurement, the pump-probe delay time was continuously scanned between -300 and 1500 fs with a step resolution of 1 fs. According to the machine parameters, the estimated FEL pulse duration was ~ 30 fs (FWHM). This was verified and confirmed by measuring an in-situ autocorrelation spectra using the delay-dependent yield of multiply charged Ar ions as the observable (see Fig. 3.10 in section 3.3).

6.3 Modelling tools

Simulations of dissociation channels

The precursor dissociation channels prepared by the pump pulse were simulated by a classical model similar to the one discussed in section 2.5. Here, we assume that the fragments reach their asymptotic velocities (v_f) with an exponential rise function [121]. The time-dependent relative velocity $v(t)$ and bond length $R(t)$ between the two fragments are approximated by,

$$v(t) = v_f \left(1 - \left(1 - \frac{v_o}{v_f} \right) \exp\left(\frac{-t}{\tau}\right) \right) \quad (6.1)$$

Where τ is the lifetime of the dissociative state which can be determined by the best fitting of final experimental data. Particularly, $\tau = 0$ means the constant velocity model which was adopted by Erk, et al. [74]. v_o and R_o are the initial relative velocity and internuclear distance between the two fragments. The asymptotic velocities (v_f) were determined by the experimental KER of the precursor dissociation channel, similar to the procedure discussed in Chapters 4 and 5. The initial configurations, i.e. v_o and R_o were sampled by a quantum harmonic oscillator which simulates the zero-point-vibration of the molecule [122] [123].

Assuming the ionization by the probe pulse does influence the kinetic energy of the fragment, finally, the density distribution of the dicationic fragment as a function of kinetic energy and delay is expressed as,

$$\rho(E, t) = [E_o + E(t)] \times [1 - P_{R_T}] \quad (6.2)$$

Where E_o is the initial internal energy by the sampling process. P_{R_T} is the ET probability which is calculated based on the COB, quantum tunneling, and the semi-classical model separately. To compare with the experiment, P_{R_T} is convoluted with the experimental uncertainty $\delta_R = \int_{-\frac{\delta_t}{2}}^{\frac{\delta_t}{2}} \frac{\partial R(t)}{\partial t} dt$ in which δ_t is the time resolution of 30 fs.

Tunneling effect

Based on the WKB approximation, the electron tunneling possibility is approximated by $e^{-2 \int_{-r_1}^{r_2} \sqrt{2[V(r)-E]} dr}$ in which $V(r)$ and E are the potential energy by the COB and the energy eigenvalue of the electron and r_i ($i = 1, 2$) are the classical turning points [124].

Semi-classical model

In terms of the thermal energy of the electron, the electron transfer rate is characterized by the reaction rate equation with formulas of the type [125],

$$K_{ET} \propto \omega e^{\frac{E_\alpha}{k_B T}} \quad (6.3)$$

where ω , E_α , k_B and T are the frequency factor, activation energy, Boltzmann constant, and temperature, respectively. Assuming the electron oscillation between the two moieties with an averaged constant velocity, the frequency factor is proportional to $\frac{1}{R}$. On the other hand, the thermal energy is replaced by the electron kinetic energy $k_B T = \frac{P^2}{2m}$. Then,

$$K_{ET} = \frac{\alpha}{R} \int_0^\infty e^{-\frac{2E_\alpha}{p^2}} \rho(p) dp \quad (6.4)$$

in which $\rho(p)$ is the momentum profile of the transferred electron which describes the possibility of finding an electron with momenta p [126]. Simply, $\rho(p)$ is only considered by the outmost molecular orbital of the neutral moiety. α is the scaling factor to normalize the possibility to 1 at the critical point. For each of the molecules, we sample 200 initial configurations. As for the precursor dissociation channels, we use Gaussian functions to fit the experimental KERs and 200 asymptotic configurations are sampled with the intensity matching the fitted profile. Mapping the initial and final configurations by Eq. (6.1 - 6.3), a total of 40 k trajectories are simulated for each of the dissociation channels. In the simulation, the charge center distance is assumed to be the same value as the center-of-mass distance.

6.4 Results and discussion

The precursor dissociation channels

The experimental KER distributions of three precursor dissociation channels of CH_2ICl are shown in Fig. 6.2. Since we do not observe any Cl^{2+} ions, we do not include the precursor channel $\text{CH}_2\text{I} + \text{Cl}^+$ here. The kinetic energies of the cationic fragments were obtained from the non-coincidence data while those of the neutral co-fragments were determined by the momentum conservation where the recoil momentum was ignored. The KER distribution of channel $\text{CH}_2\text{Cl}^+ + \text{I}$ is almost peaked at 0 eV while the peaks of $\text{CH}_2\text{I}^+ + \text{Cl}$ and $\text{CH}_2\text{Cl} + \text{I}^+$ are 0.05 and 0.07 eV, respectively. The smaller peak value and sharper distribution indicate that the potential energy surface of the former channel is smoother than the others. In this situation, the lifetime of channel $\text{CH}_2\text{Cl}^+ + \text{I}$ is expected longer than channel $\text{CH}_2\text{Cl} + \text{I}^+$ and $\text{CH}_2\text{I}^+ + \text{Cl}$ while that of the latter channels are similar to each other. In the simulation, the constant velocity gives very good descriptions of $\text{CH}_2\text{Cl} + \text{I}^+$ and $\text{CH}_2\text{I}^+ + \text{Cl}$. This is the same model used in the work of [74] for C-I bond breaking and leading to I^+ precursor dissociation limit. For channel $\text{CH}_2\text{Cl}^+ + \text{I}$, a lifetime of 200 fs provides a good description.

Being further ionized by the probe pulse, the precursor channels can dissociate into either a neutral-dication channel that is of interest for this work or a competing monocation-monocation channel. The latter one could also be created by the ET in the neutral-dication channel. The KERs as a function of delay for the CE of monocation-monocation channels are shown in Fig. 6.2 (b) for C-I and Fig. 6.2 (c) for C-Cl bond dissociation. Similar to this kind of plots presented in Chapters 4 and 5, two distinct features can be distinguished. On one hand, the delay-independent bands centered at 4.5 eV for $\text{CH}_2\text{Cl}^+ + \text{I}^+$ and 3.8 eV for $\text{CH}_2\text{I}^+ + \text{Cl}^+$ originate from the double ionization by the probe pulse and the following CE. On the other hand, the delay-dependent bands with asymptotic KER both centered at about 1 eV originate from the target that is first created into precursor channels $\text{CH}_2\text{Cl} + \text{I}^+$ or $\text{CH}_2\text{Cl}^+ + \text{I}$ in Fig. 6.2(b) and $\text{CH}_2\text{I}^+ + \text{Cl}$ in Fig. 6.2 (c), and then is further singly-ionized at a certain delay. As discussed earlier, the constant velocity model is adopted for CH_2Cl

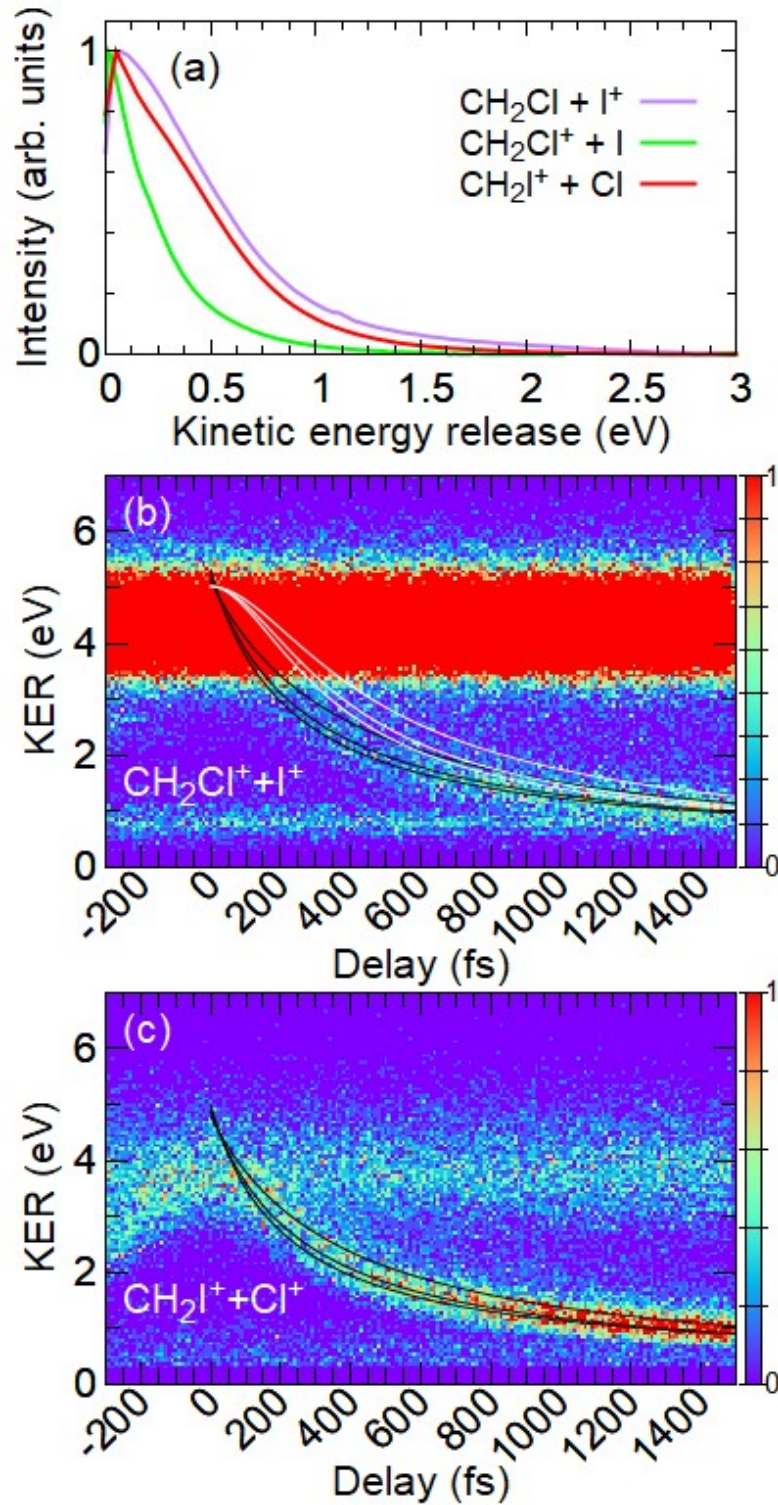


Figure 6.2: (a) Kinetic energy releases (KER) of the three precursor dissociation channels of CH_2ICl recalculated from the measured KE of non-coincident singly charged fragments. Kinetic energy releases of the Coulomb explosion channels for C-I (b) and C-Cl (c) bond dissociation. In (b) and (c) the black lines correspond to the constant velocity model ($\tau = 0$ fs). The white lines correspond to a lifetime of $\tau = 200$ fs. From bottom to top, the same-color lines correspond to asymptotic kinetic energy releases of 0.3, 0.2, and 0.1 eV, respectively.

+ I^+ and $\text{CH}_2\text{I}^+ + \text{Cl}$. Adding the Coulombic potential at a certain internuclear distance, the simulated KERs as a function of delay are shown by the black curves in Fig. 6.2 (b) and (c) with three asymptotic KERs of 0.3, 0.2, and 0.1 eV. The white curves in Fig. 6.2 (b) represent the simulated KERs with a dissociation time of $\tau = 200$ fs. The constant velocity model agrees well with the experiment. As for $\text{CH}_2\text{Cl}^+ + \text{I}$ precursor channel, the simulated KERs (white curves) are roughly in the range of the experimental band. The branching ratio of $\text{CH}_2\text{Cl} + \text{I}^+$ and $\text{CH}_2\text{I}^+ + \text{Cl}$ channels also influences the agreement. According to the measured non-coincident TOF spectra, $\text{CH}_2\text{Cl} + \text{I}^+$ is the dominant channel.

Charge transfer in CH_2ICl

Fig. 6.3 (a) shows the experimental kinetic energy distribution for the dicationic species I^{2+} as a function of the time delay between the EUV pump and probe pulses. Three distinct features marked by 1, 2, and 3 can be distinguished. The high energy (centered at ~ 2.3 eV) delay-independent band 1 comes from triple ionization of the target, where the molecule remains bound after the pump pulse in some intermediate charge state, and dissociates into $\text{CH}_2\text{Cl}^+ + \text{I}^{2+}$ final state after the probe pulse. The delay-dependent band 2 with asymptotical kinetic energy centered at 1.3 eV originates from the target that is first double ionized by the pump pulse by absorbing two photons leading to a CE channel $\text{CH}_2\text{Cl}^+ + \text{I}^+$ and further ionized by the probe pulse at a certain delay. In this situation, the internuclear distance before the CE increases with the pump-probe delay, which is reflected by the decreasing kinetic energy. The experimental asymptotical kinetic energy of the I^{2+} fragment from the $\text{CH}_2\text{Cl}^+ + \text{I}^+$ channel is ~ 1.25 eV in this work indicating that $\text{CH}_2\text{Cl}^+ + \text{I}^+$ is the precursor dissociation channel for band 2 in Fig. 6.3 (a). These assignments are consistent with the measured delay-dependent KERs of the coincident $\text{CH}_2\text{Cl}^+ + \text{I}^{2+}$ channel (not shown). Within the constant velocity model, and adding the Coulombic energy at a certain delay, $\frac{2}{R(t)}$, we simulate the kinetic energy as a function of delay of band 2, as shown by the orange curve in Fig. 6.3 (a).

Band 3 with the lowest kinetic energy is the most interesting one for this work. On one

hand, the center value of the kinetic energy is almost a constant of 0.069 eV. On the other hand, the event counts show a delay-dependent character where nearby zero-delay produces the lowest intensity which is increasing with delay. In this case, the target is single ionized by the EUV pump pulse leading to a neutral-cation precursor dissociation channel $\text{CH}_2\text{Cl} + \text{I}^+$. During the dissociation, the iodine ion is further ionized by the probe EUV pulse to $[\text{CH}_2\text{Cl} + \text{I}^{2+}]$ state. This state could dissociate directly into $\text{CH}_2\text{Cl} + \text{I}^{2+}$. In this case, ignoring the influence on the kinetic energy from the second ionization process, the asymptotical KER is the same as that of the precursor dissociation channels which is shown by the purple curves in Fig. 6.2. At short internuclear distances, the electron could be transferred from CH_2Cl to I^{2+} resulting in dissociation limit $\text{CH}_2\text{Cl}^+ + \text{I}^+$ and, of course, decrease the intensity of I^{2+} production.

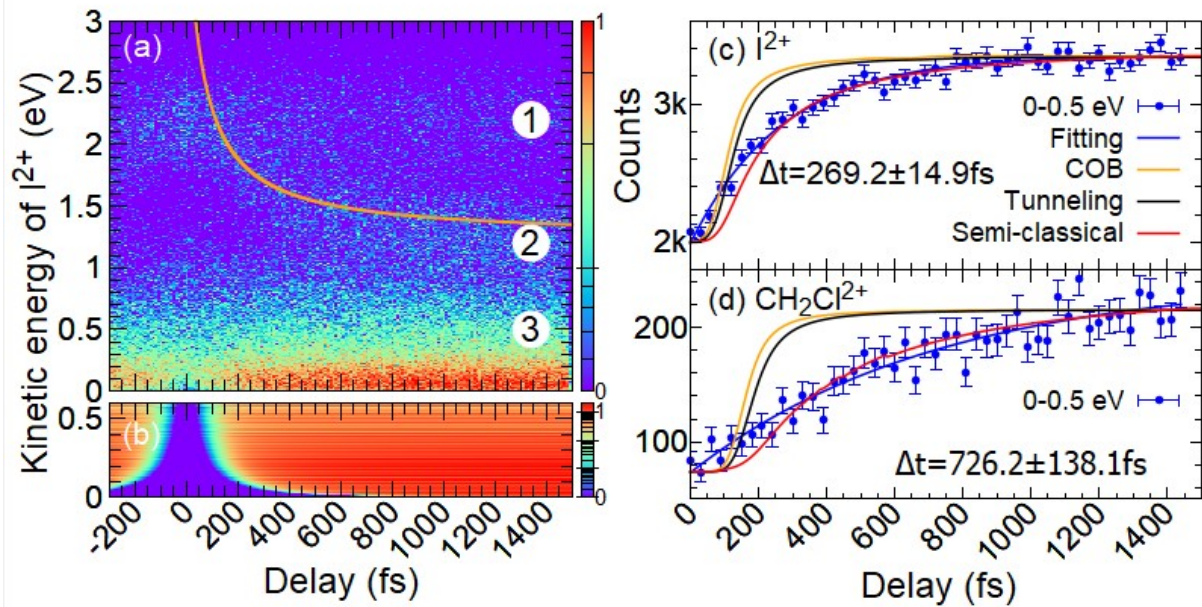


Figure 6.3: Map of the delay-dependent kinetic energy distribution of dicationic ions from the dissociation of CH_2ICl . Experimental (a) and simulated (b) two-dimensional map of I^{2+} . Projection of the two-dimensional map with low kinetic energy conditions for I^{2+} (c) and $\text{CH}_2\text{Cl}^{2+}$ (d).

The experimental yields of low energy I^{2+} (0 - 0.5 eV) as a function of delay is shown by the solid blue circles. The blue curve represents the fitting result by an exponential function, $y = y_o + A \times \exp[-\frac{(t-t_o)}{\Delta t}]$. Within the experimental uncertainty, the fitted time-delay for ET is essentially zero.. This means that even at a short internuclear distance the

ET probability is not saturated which is different from the x-ray probe experiments [74] [76]. The ET probability decreases with increasing delay and disappears at the delay larger than 800 fs. The critical distance R_c calculated by the COB model of state $[\text{CH}_2\text{Cl} + \text{I}^{2+}]$ is 6.3 Å. In terms of simulation, we first simulate the two-dimensional map similar to Fig. 6.3 (a) and project the kinetic energy with the same energy window to one-dimensional yields of I^{2+} as a function of delay. The two-dimensional map resulting from the semi-classical model is shown in Fig. 6.3 (b). Generally, the delay-dependent feature is reproduced by the simulation. At zero delay, the lowest intensity is observed. At the lowest kinetic energy, the intensity increases with delay and stays constant at delays larger than 800 fs. For short delays, the onset time decreases with increasing energy. This is understandable since higher kinetic energy means a faster dissociation. Therefore, the ET is inhibited at a shorter delay.

There are differences in the kinetic energy between the experiment and simulation. While the signal intensity in the experiment decreases quickly at the energy larger than 0.2 eV, the simulation shows a broad distribution. This might be due to the KER difference in channels $\text{CH}_2\text{Cl} + \text{I}^{2+}$ and $\text{CH}_2\text{Cl} + \text{I}^+$. The experimental kinetic energy of I^{2+} indicates that the KER of $\text{CH}_2\text{Cl} + \text{I}^{2+}$ has a very sharp distribution, which corresponds to the lower-energy part of the purple curve in Fig. 6.2 (a). The experimental precursor KER we used here corresponds to the full profile of the purple curve in Fig. 6.2 (a).

The simulated yields of I^{2+} as a function of delay by three models, COB, tunneling, and semi-classical models, are shown by the orange, black, and red curves in Fig. 6.3 (c). Obviously, the semi-classical model gives the best description. Both COB and tunneling models deviate from the experiment at the delays smaller than 800 fs. Still, deviations between the three models and the experiment are observed at very short delays. The ET probability is saturated at the short delay (< 50 fs). This is because in our simulation the ET probability is 100% within the critical distance. On the other hand, in our simulation ET probability is 0 outside the critical distance which results in a quickly disappeared ET with the increasing delay of the COB model. The overall agreement between semi-classical simulation indicates that the ET at a distance larger than R_C can be considered within the framework of a thermal dynamics model, where the thermal energy of the electron gives it

a chance to cross the potential barrier.

The yields of $\text{CH}_2\text{Cl}^{2+}$ as a function of delay of the slower precursor dissociation channel $\text{CH}_2\text{Cl}^+ + \text{I}$ is shown in Fig. 6.3 (d). Here, the critical distance $R_C = 5.27 \text{ \AA}$ is shorter than for the previous channel, which is to some extent balanced by the slower dissociation. The results show that the slow dissociation plays a dominant role. Both the experiment and simulations show that the yields for this channel increase slower with delay compared to I^{2+} signal discussed above, in accordance with the slower dissociation. In this channel, the experimental onset time is also zero within the experimental uncertainty. The simulated onset time is about 100 fs, which disagrees with the experiment. At a long delay, a very good agreement is achieved between the semi-classical model and the experiment.

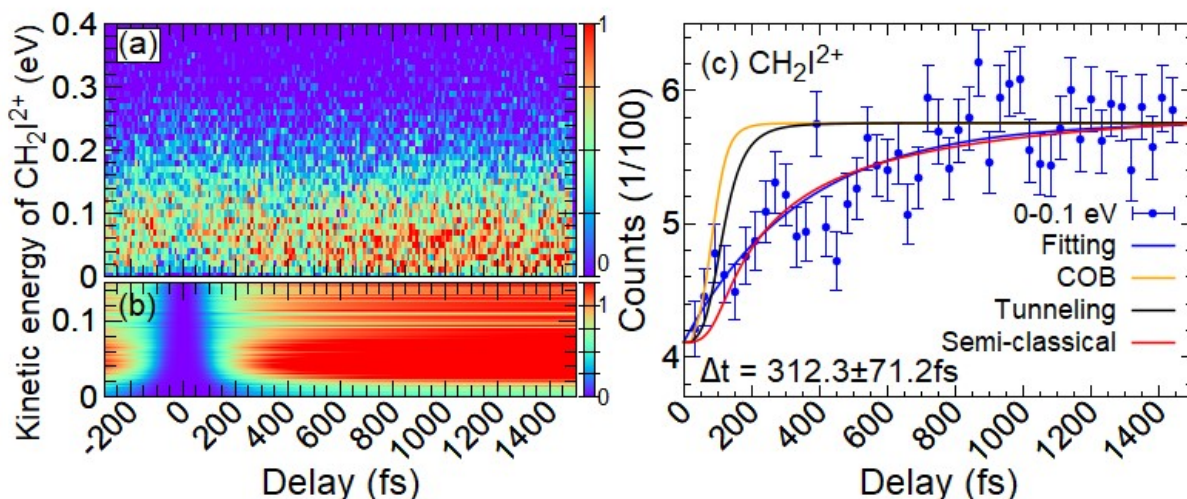


Figure 6.4: (a) Two-dimensional map of the delay-dependent kinetic energy distribution of $\text{CH}_2\text{I}_2^{2+}$ from the dissociation of CH_2ICl . (b) Projection of the two-dimensional map onto the delay axis for low kinetic energy conditions of 0 - 0.1 eV.

The measured two-dimensional map of the delay-dependent kinetic energy distribution of $\text{CH}_2\text{I}_2^{2+}$ from the dissociation of CH_2ICl is shown in Fig. 6.4 (a). Similar behavior as I^{2+} is observed. In this channel, the critical distance is $4.25 \text{ \AA}$. Therefore, the signatures of the ET is expected to quickly disappear with the time delay. As a result, the simulated curves show the onset time which is less than 50 fs. This is also deviating from the experiment, which shows zero onset time within the experimental uncertainty.

Charge transfer in CH₃I

We only observe one ET channel from the dissociation of CH₃I, i.e. ET from CH₃ to I²⁺. Here, a constant velocity model is adopted as in Erk et al. [74]. The KER of the precursor dissociation channel CH₃ + I⁺ is described by a Gaussian profile with a peak at 0.66 eV corresponding to I⁺ energy of 0.07 eV [47] and a width at half maximum of 1 eV. The measured two-dimensional map of the delay-dependent kinetic energy distribution of I²⁺ is shown in Fig. 6.5 (a). At the short delay, the two-dimensional map shows evidence that with increasing kinetic energy the events extent towards zero delay. This phenomenon is even clearer in the simulated two-dimensional map, as shown in Fig. 6.5 (b).

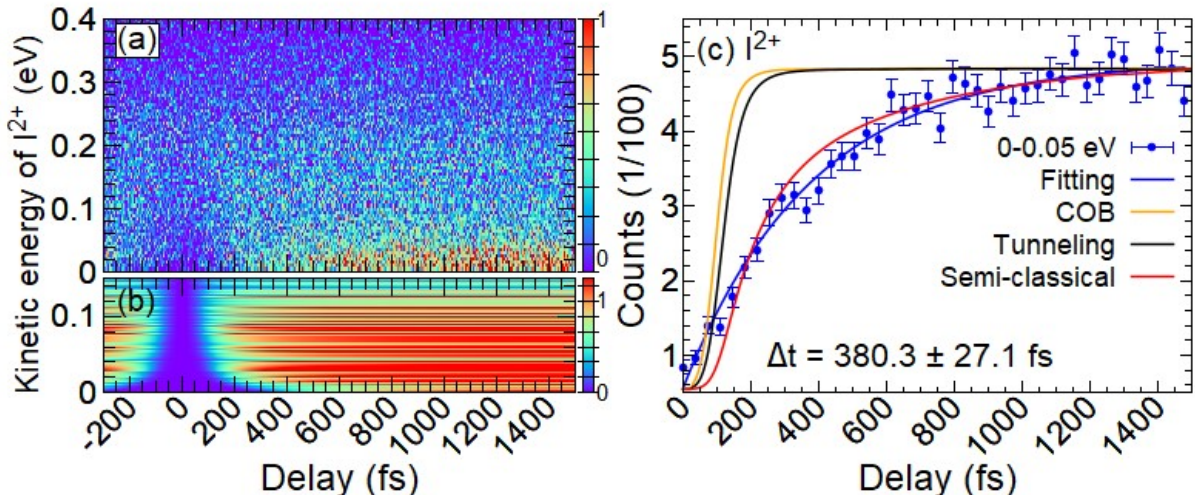


Figure 6.5: (a) Two-dimensional map of the delay-dependent kinetic energy distribution of I²⁺ from the dissociation of CH₃I. (b) Projection of the two-dimensional map with low kinetic energy conditions of 0 - 0.05 eV.

The potential energy surface analysis [127] [128] [24] shows that the most probable state corresponding to the precursor dissociation channel CH₃ + I⁺ is $\tilde{A}$, which is created by removing a C-I covalent bond electron. In this state, the potential of the inner turning point of the Frank-Condon region is higher than the dissociation limit. The quantum vibrational wavepacket simulation of Malakar et .al [24] showed that within 100 fs C-I bond has a small possibility to go beyond 9 a.u.. At this bond length, the molecular orbital overlap between CH₃ and I⁺ is very small. Therefore, the C-I bond could be broken without intramolecular attraction. Considering the molecular internal energy, the molecule could dissociate even

faster. This suggests that the constant velocity model of C-I bond dissociation is a good approximation [74]. The results of the one-dimensional yields of I^{2+} are shown in Fig. 6.5 (c). Same as the aforementioned channels, the COB, and tunneling model overestimated the yields at short delay while the semi-classical model gives the best description. Near zero delays, the experimental onset time is essentially zero, which cannot be reproduced by any of the three models.

Comparing all of the simulations with the experiment, the deviation is always observed at short delays, i.e. within the critical distance. It is clear in our simulation that the ET probability is 100% within critical distance. The deviation indicates that the situation under short internuclear distance is much more complicated and the quantum effects cannot be ignored. For example, the covalent bond of C-I is formed by carbon 2s-2p hybrid orbital and one iodine 5p orbital, $\psi_{C-I} = \alpha \psi_c + \beta \psi_I$ where α and β are the orbital coefficients. In the covalent orbital, the electron is delocalized. After the probe pulse, if the covalent electron is not fully removed, the molecular orbital delocalization could lead to a decreased effective charge state of the electron donor, i.e. $p' < 1$ in Eq. 6.3 and 6.4. This results in a shorter critical distance according to eq. 6.4. At a short internuclear distance, it is impossible to create purely localized charges by valence ionization. Based on the adiabatic picture, the dissociation limit is determined by the initial electronic state in the Frank-Condon region. Some of them can dissociate into neutral-dication limit. In short, the probability of ET limit cannot be guaranteed to be 100% at a short delay by valence ionization. In other words, the dicationic molecule formed at a short internuclear distance is a molecule and cannot be treated as individual atoms in any way.

6.5 Conclusion

In conclusion, we performed a XUV pump – XUV probe experiment utilizing the FLASH2 FEL facility by means of a reaction microscope. The ultrafast intramolecular electron transfer due to valence ionization of halomethane molecules chloriodomethane and iodomethane was investigated. The charge transfer is traced by the yields of the dicationic species as a

function of delay. We observe a pronounced charge transfer possibility at a long internuclear distance which cannot be explained by the classical over-the-barrier model. We find that the electron tunneling effect improves the description, however, still not enough. Based on the reaction rate equation, we develop a semi-classical model in which the thermal energy of the electron gives it a chance to cross the potential barrier, and a fairly good agreement with the experiment is achieved. Within a short internuclear distance, all of the simulations cannot reproduce the experiment which shows no saturated charge transfer possibility. Based on this comparison, we assume that this phenomenon is essentially due to the molecular orbital delocalization which is not compatible 100% monocation-monocation dissociation limit for molecular dication.

Chapter 7

Conclusion and outlook

In this thesis, a femtosecond pump-probe experimental scheme combined with coincident ion momentum imaging technique has been applied to study photo-induced processes in small polyatomic molecules, halomethanes. This study covered three basic regimes of light-matter interaction – single- and few-photon excitation at UV wavelengths, strong-field processes in the near-infrared domain and single-photon XUV ionization. The work presented here mainly focused on visualizing and understanding nuclear dynamics, without necessarily specifying the electronic states involved.

The strong-field part of this work addressed two complementary objectives. First, it provided a detailed overview of strong-field driven processes in two di-halomethane molecules, CH_2I_2 and CH_2ICl . In particular, we demonstrated the role of different vibrational modes in ionization and fragmentation of di-halomethanes, and showed how the elimination of molecular halogen ion (I_2^+ or ICl^+) can be correlated with vibrational motion in either ionic or neutral state, depending on the intensity of the probe pulse employed. Furthermore, we mapped the formation of molecular halogens in both systems using two- and three-body breakup schemes and laser-induced Coulomb explosion imaging (CEI), and demonstrating the dominance of direct elimination channels and providing evidences supporting the formation of neutral molecular halogen, which was not directly observed. Second, we used these dynamics as test grounds for developing and refining our imaging schemes and analysis tools,

in particular, for three-particle coincident CEI with intense NIR laser as a probe.

As a next step, this technique and analysis have been employed to study UV-driven dynamics in diiodomethane. Here, we focused on four basic photochemical processes: (1) dissociation breaking one of the carbon-halogen bonds; (2) transient photoisomerization creating a short-lived “linearized” $\text{CH}_2\text{I-I}$ isomer; (3) molecular I_2 elimination; and (4) three-body dissociation. While the former two channels are mainly driven by the absorption of a single UV photon, the latter two are dominated by the two-photon or higher-order transitions. For C-I bond cleavage resulting in CH_2I and I fragments, we confirmed that our imaging approach yields the same translational energies as the other techniques (like transient absorption or velocity map imaging), and demonstrated the role of CH_2 co-fragment rotation in such a reaction. We observed clear signatures of the formation of the short-lived transient $\text{CH}_2\text{I-I}$ isomer, which was debated for the gas phase [35],[34], and determined its formation time to be of order of 75 fs and 115 fs, respectively. While the I_2 elimination was found to be dominated by the direct, “synchronous” mechanism, driven by two- or-three photon absorption, we found some evidence supporting a competing single-photon pathway proceeding via isomerization and subsequent I_2 detachment. Finally, we observed clear signatures of three-body dissociation, triggered by two-photon absorption, most likely proceeding via initial excitation to one of the Rydberg states. Here it should be noted that while the neutral three-body dissociation channels are usually hard to access experimentally [53], [54], [55], they can be easily separated in our triple-coincidence measurements.

Finally, we applied the knowledge and experience in imaging two-body molecular dissociation to explore the relation between the dissociation and electron transfer processes in CH_3I and CH_2ICl molecules ionized and dissociated by XUV light. These experiments, carried out at FLAS-II FEL facility in Germany and employing valence XUV ionization to create charge imbalance, provided a complimentary view for a series of recent FEL-based studies of charge transfer upon inner-shell photoabsorption [74]. Our results suggest the existence of a rather long-range charge transfer and clearly highlight that a classical over-the-barrier model, which was successfully employed to describe many inner-shell studies, fails completely in a limit of relatively low charge states and small internuclear separations.

The approach employed here has several serious limitations. The first one is the above-mentioned insensitivity to the electronic states involved. Therefore, ideally, such a measurement needs to be complemented by one of the spectroscopic ultrafast tools, like photoelectron spectroscopy or transient absorption. A promising approach here would be also combining ion and electron measurements in a coincidence mode, which, however, appears to be more efficient with short wavelength sources [17]. The second limitation is the complexity of the probe step itself, i.e., of laser-induced multiple ionization and Coulomb explosion. If a detailed theoretical modelling of the probe step would be needed, that might constitute a serious bottleneck. The way to circumvent it would be to use even shorter pulses of higher intensity, such that the probing probability saturates and approaches unity. Finally, for NIR wavelengths, another big issue is that high charge states of interest constitute a very small fraction of the total ionization yield. Along with the requirement to have less than one event for each laser shot, this makes such experiments technically challenging. Increasing the repetition rate of the sources might help here, like a planned acquisition of a 100 kHz laser system at the JRML. Moreover, this problem was recently shown to be less of an issue for intense X-ray pulses, where the fraction of highly charged states upon multiple inner-shell absorptions and Auger decays becomes much larger [129].

Finally, last but not least the study of this kind requires connection with theory. This particularly applies to a pump step, where modern quantum chemistry toolbox provides a variety of approaches for modeling dynamics upon photoexcitation. Although only limited progress in this direction was achieved in this thesis, the collaborative work with the group of Loren Greenman and with Enliang Wang is underway to model UV-driven dynamics in halomethanes directly relevant to this study.

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Appendix A

Estimation of temperature of a molecular jet in COLTRIMS

It is essential to know the temperature of the molecular target in the experiments carried out in COLTRIMS. For this, we used the experimentally measured time-of-flight(TOF) and (x,y) positions of parent (CH_2I_2^+) ions by the COLTRIMS system for two cases: (a) Without carrier and (b) With He as a carrier. The 2D position (X vs Y) plot and the 1D TOF plot of parent ions is shown in fig. A.1 (a) and Fig. A.1 (b) respectively. To estimate the target temperature, it is important to select the parent ion from the cold region of the target. It is obtained by imposing the condition on the XY plot and the TOF plot. The conditions are represented by the polygonal dashed region on the XY plot and the two vertical dashed lines in the TOF plot.

For determining the temperature, we take the momentum distribution (P_y) of the parent ion along the y-direction, which is the direction of jet propagation. The conditions mentioned above are imposed on the momentum distribution of parent ions along the y-direction. Thus, obtained momentum distribution is fitted with Maxwell-Boltzmann distribution ($\propto \exp(\frac{-P_y^2}{2mKT})$), where K is Boltzmann constant, and T is the temperature of the jet to be estimated. The jet temperature is estimated to be 45.56 K for the experiment without using a carrier, while it is found to be 45.85 K for the experiment with Helium as a carrier. So, the

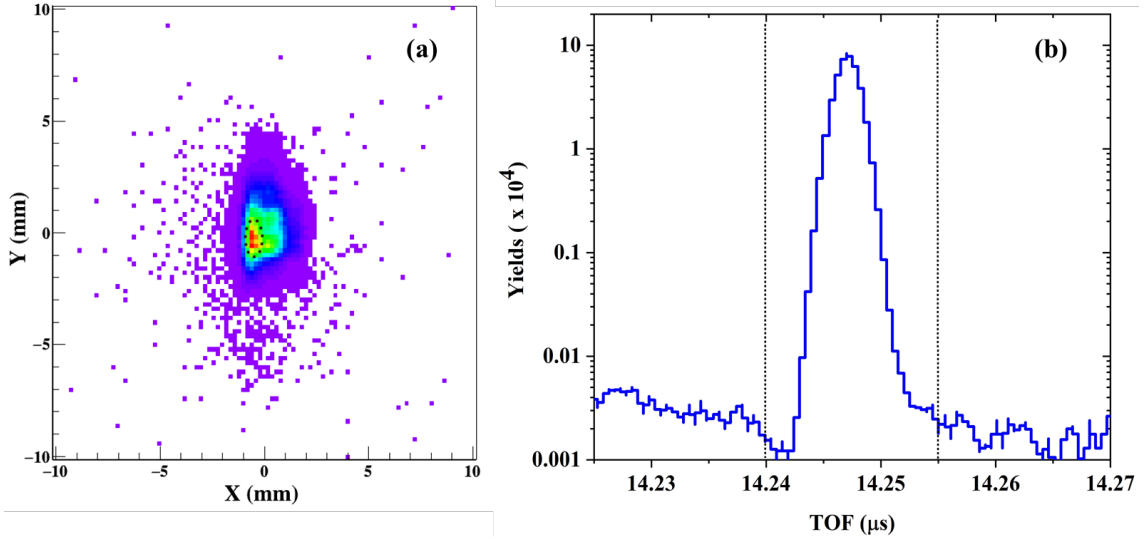


Figure A.1: (a) 2D map X vs Y plot and (b) 1D time-of-flight (TOF) plot for CH_2I_2^+ ions without carrier. The polygonal dashed region on XY plot and dashed vertical lines in TOF plot are conditions imposed in momentum distribution (P_y) of parent ion along y-direction for the estimation of temperature.

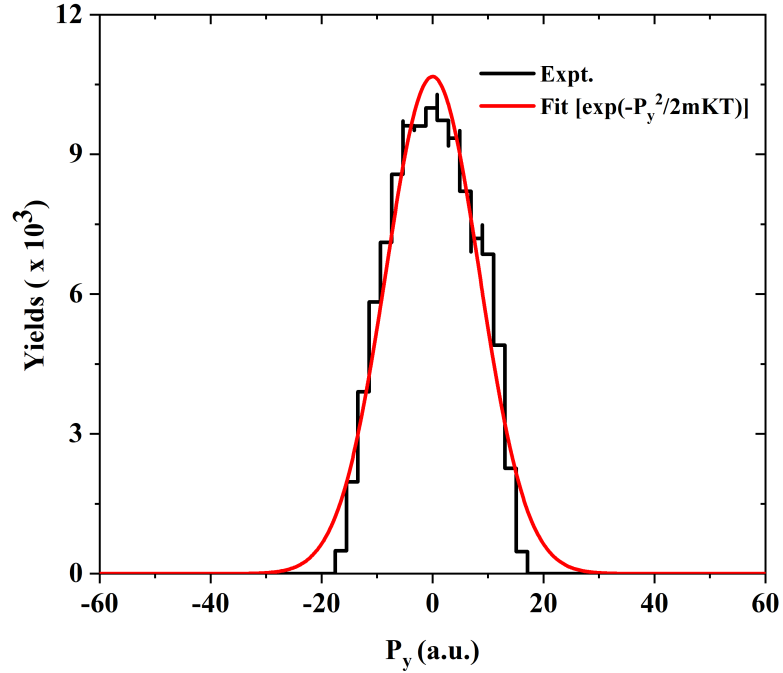


Figure A.2: The momenta distribution of parent ion along y-direction which is the jet propagation direction. For obtaining this momentum distribution, conditions shown in A.1 is imposed. The resulting momentum distribution is fitted with Maxwell-Boltzman distribution to obtain temperature of molecular target.

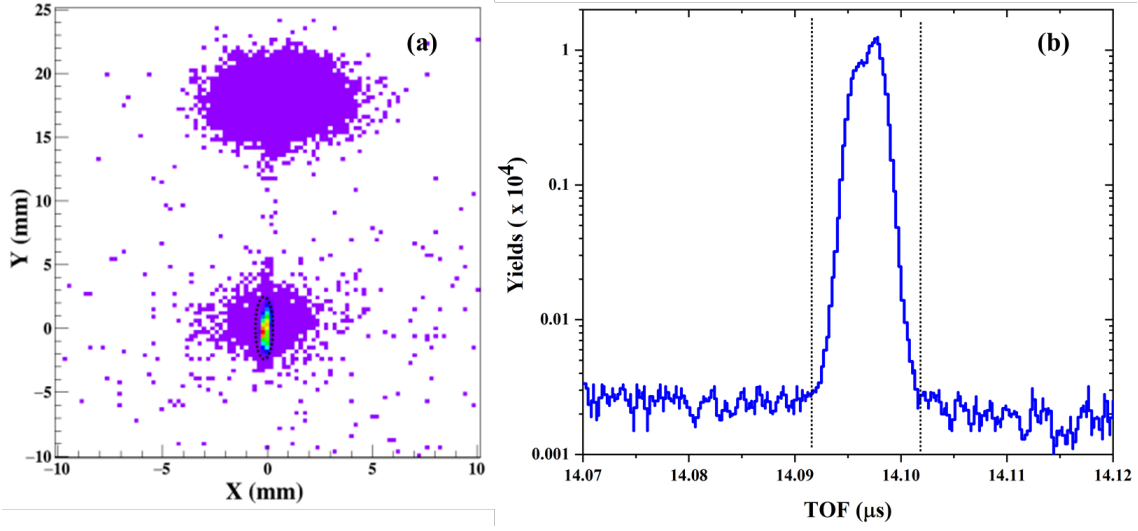


Figure A.3: (a) 2D map X vs Y plot and (b) 1D time-of-flight (TOF) plot for CH_2I_2^+ ions with Helium as carrier. The polygonal dashed region on XY plot and dashed vertical lines in TOF plot are conditions imposed in momentum distribution (P_y) of parent ion along y-direction for the estimation of temperature.

carrier is only increasing the flow of the molecular target.

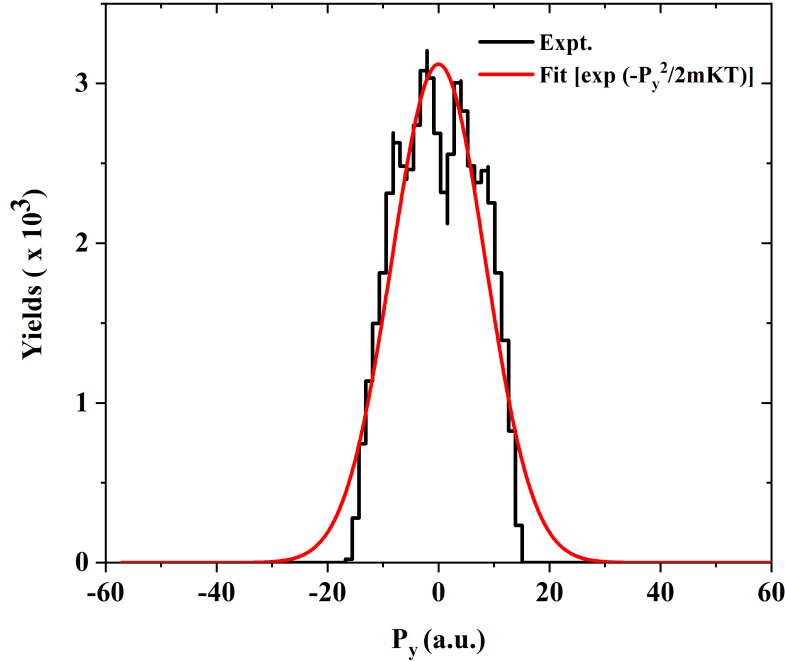


Figure A.4: The momenta distribution of parent ion along y-direction which is the jet propagation direction. For obtaining this momentum distribution, conditions shown in A.1 is imposed. The resulting momentum distribution is fitted with Maxwell-Boltzman distribution to obtain temperature of molecular target.

Estimation of the population in vibrational energy levels at a temperature

We tried to estimate the population in vibrational energy levels in the parent molecule for the given temperature of the molecular target. The molecular partition function (q) estimates the number of states that are thermally accessible to a molecule at the temperature of the system. This function is expected to increase from 1 at $T = 0$ and approaches infinity as T tends to ∞ . temperature. At very low temperatures, where q is close to 1, only the lowest state is significantly populated. As the temperature is raised, the population breaks out of the lowest state, and the upper states become progressively more highly populated. The name 'partition function' reflects the sense in which q measures how the total number of molecules is distributed over the available states.

The molecular partition function can be expressed as:

$$q = \frac{1}{1 - \exp(-\beta\epsilon)} \quad (\text{A.1})$$

where, $\beta = \frac{1}{KT}$ and ϵ is vibrational energy level spacing. The fraction of molecules in the state ν with energy ϵ_ν is,

$$p_\nu = \frac{\exp(-\beta\epsilon_\nu)}{q} \quad (\text{A.2})$$

where ν is quantum number of the vibrational states and $\epsilon_\nu = \nu\epsilon$. For ground state i.e. $\nu = 0$,

$$p_0 = 1 - \exp(-\beta\epsilon) \quad (\text{A.3})$$

For the ground electronic state of neutral CH_2I_2 molecule, the values of I-C-I bending mode and C-I stretching mode is 121 cm^{-1} and 486 cm^{-1} respectively [69]. The jet temperature is taken to be 45.56 K as estimated from the experimental data without carrier gas. Based on this information, the $\beta\epsilon$ values are calculated for the vibrational modes. For I-C-I bending mode, $\beta\epsilon \sim 3.82$. So, the p_0 value is 0.978. Similarly, for the C-I stretching mode, the $\beta\epsilon$ value is calculated to be ~ 15.35 , and the q value corresponding to the mode is found to be 0.99. Both of these values mean that the population is mostly in the ground vibrational state. Still, there might be % of the population in $\nu = 1$ for bending. That's not

much, but not negligible. Moreover, it is easier to get a double frequency if we start with a mixture of $v=0$ and $v=1$ than if we would have nothing at $v=1$ because we have more ways to get to $v=2$.

Appendix B

Estimation of laser intensity in COLTRIMS

For linearly polarized light, direct electrons without any scattering, can have maximum possible energy $2U_p$ ($2U_p$ “plateau”), where U_p is the pondermotive energy. This maximum possible energy is displayed as a characteristic kink at the corresponding recoil momentum value [130] [113]. We use this kink feature, which represents the transition from direct to rescattered electrons, in the Ne^+ ion momentum distribution to calibrate the peak laser intensity. In other words, absolute calibration of the peak intensity corresponds to the maximum drift momentum of $2\sqrt{U_p}$ that electrons can gain from the laser field.

For the momentum measurement of Ne^+ , a weak electric (say 1 Vcm^{-1}) and magnetic (say 5 G) fields were applied along the laser polarization axis to guide ions and electrons to the time and position-sensitive channel plate detectors. From the time (t) and position (x,y) information, the full momentum vectors of coincident ions and electrons were calculated. Neglecting the small momentum of the absorbed photons, momentum conservation was ensured for each single event. For the intensity calibration of IR laser pulses (say power of 150 mW), the $2U_p$ (as shown by dashed lines) and $10U_p$ values from the P_z distribution of Ne^+ is taken under cold jet condition. Then, the laser intensity (I) is equal to the $4 U_p \omega^2$ where $2\sqrt{U_p} = P_z$ and ω is angular frequency.

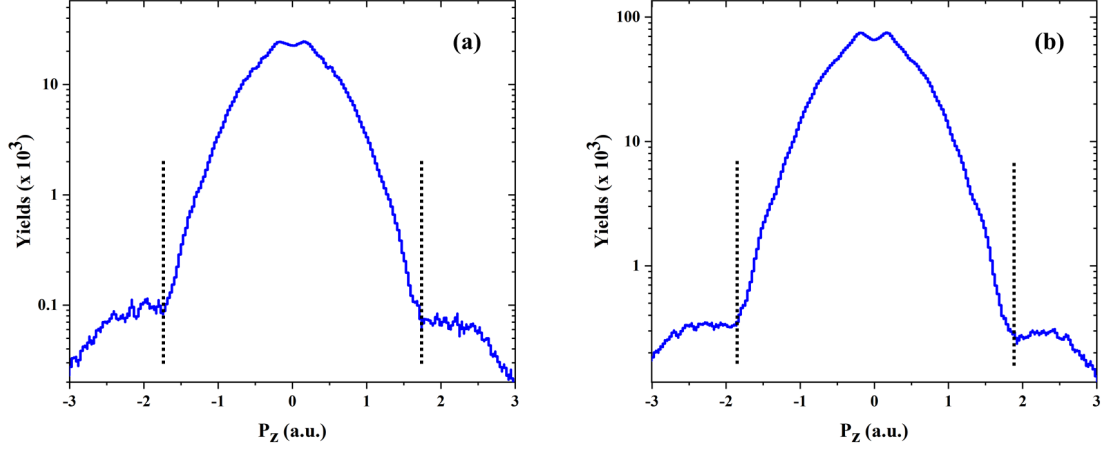


Figure B.1: (a) 2D map X vs Y plot and (b) 1D time-of-flight (TOF) plot for CH_2I_2^+ ions without carrier. The polygonal dashed region on XY plot and dashed vertical lines in TOF plot are conditions imposed in momentum distribution (P_y) of parent ion along y-direction for the estimation of temperature.