

Characterising the Photodissociation Dynamics of Few-Atom Systems Via X-ray Coulomb Explosion Imaging

James Francis Unwin

Hertford College
University of Oxford

*A thesis submitted for the degree of
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Abstract

Coulomb explosion imaging has shown promise as a technique to study ultrafast chemical reactions. When a molecule undergoes a Coulomb explosion, it fragments into multiple charged ions, with their geometry fixed in the configuration at the time of the explosion. Analysis of the positions and momenta of these resultant ionic fragments allows determination of the molecular structure prior to explosion. By varying the time between initiation of a reaction, and when it is Coulomb exploded, the evolution of molecular dynamics can be followed.

This thesis demonstrates Coulomb explosion imaging's capability to characterise a wide variety of different dissociation properties. This is accomplished by following the photodissociation dynamics of three molecules. In each case, photoexcitation and dissociation is initiated via an ultraviolet pulse, with either an infrared or X-ray pulse initiating the Coulomb explosion.

CH_2BrI is used to show that comparison of the experimental data to that predicted by a classical over-the-barrier model can determine that at 200 nm the primary dissociation occurs via a three-, rather than two-body mechanism. Additionally, within this three-body mechanism, which of the resultant fragments are charged is identified.

The $\text{C}_6\text{H}_5\text{I}$ data is used to demonstrate that Coulomb explosion imaging can isolate and identify the signals produced from two overlapping dissociation channels. These two channels are found to produce the same molecular cofragments, but each residing in a different electronic state. Comparison to an over-the-barrier model again enables the identification of this electronic state.

The dissociation of CS_2 is used to show Coulomb explosion imaging's sensitivity to nuclear motion on a transient excited state. By utilising a combination of simple modelling, and covariance analysis, the degree of bending undergone by the molecule prior to dissociation is identified.

These explored dissociations demonstrate that CEI is a widely applicable tool for the characterisation of ultrafast chemical reactions.

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List of Abbreviations

1D, 2D, 3D	One-, Two- or Three-Dimensional
APD	Avalanche PhotoDiode
BBO	BaB ₂ O ₄
CDF	Cumulative Distribution Function
CEI	Coulomb Explosion Imaging
CMOS	Complementary Metal-Oxide Semiconductor
CPA	Chirped-Pulse Amplification
CT	Charge Transfer
FEL	Free Electron Laser
FLASH	Free electron LASer at Hamburg
FROG	Frequency-Resolved Optical Gating
FWHM	Full Width at Half Maximum
GF	Global Fitting
IDL	IDLer pulse
IP	Ionisation Potential
IR	InfraRed
KE	Kinetic Energy
MCP	Micro Channel Plate
NIR	Near-InfraRed
OTB	Over-The-Barrier
OTBI	Over-The-Barrier Ionisation
PEC	Potential Energy Curve
PES	Potential Energy Surface
Ph	Phenyl
PImMS	Pixel Imaging Mass Spectrometer

SACLA		the SPring-8 Angstrom Compact free electron LAser
regen		Regenerative-Amplifier
RF		RadioFrequency
SASE		Self-Amplified Spontaneous Emission
SF		Sum Frequency generation
SFA		Strong-Field Approximation
SH		Second Harmonic
SIG		Signal Pulse
ToA		Time-of-Arrival
ToF		Time-of-Flight
TOPAS		Tuneable Optical Parametric Amplifier System
ToT		Time-over-Threshold
Tpx3		Timepix3
UV		UltraViolet
VID		Vacuum Imaging Detector
VMI		Velocity Map Imaging
XUV		eXtreme UltraViolet

1

Introduction

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1.1 Motivation and Context

Photochemical reactions, in part due to their relevance to daily life (such as in the processes of photosynthesis and ozone depletion), are the source of much study[1–3]. These reactions readily occur day-to-day due to the UltraViolet (UV) component of sunlight, and they receive much attention in the fields of chemistry, biology, medicine and molecular physics[4]. After a molecule interacts with and absorbs a photon, it can undergo complicated chemistry due to significant electronic and structural rearrangements, often prior to dissociation. The ability to follow these reactions, and build a picture of their operation, is important to further our understanding of complicated biological and photochemical processes. One of the long-term goals of molecular physics and chemistry is to develop a variety of methods that can follow nuclear dynamics with such specificity that motion between individual quantum

states can be observed. The ability to follow migrations between states can become increasingly complicated as the energy of the excitation photon increases, as the higher excitation energy allows access to additional higher-lying and overlapping states. This thesis explores how Coulomb Explosion Imaging (CEI) can be used to follow these complicated photochemical reactions, and how it can complement information obtained via existing analysis methods.

Many photochemical reactions occur over ultrafast (sub-picosecond) timescales, with molecules undergoing complex structural changes, further complicating the extraction of information about the nature of the excitation. As such, having as large a toolbox of spectroscopic and analytical techniques as possible is important to enable a full accounting of the reaction dynamics. The development of ultrafast femtosecond lasers has led to the creation of multiple experimental methods that are able to follow these reactions from the ground state into the excited state and through to the final products. Techniques such as time-resolved photoelectron spectroscopy, ultrafast X-ray/electron diffraction, and time-resolved X-ray absorption spectroscopy have all proven useful in examining the electronic and nuclear dynamics of many photochemical reactions[5–7]. Photoelectron spectroscopy relies on the photoelectric effect (the fact that a molecule emits electrons upon interaction with electromagnetic radiation) to determine the nature of emitted electrons. The produced photoelectrons have different energies depending on the electronic and vibrational states they are emitted from. As such, comparison of the energies of the detected photoelectrons allows their excited state of origin to be determined[5]. Rather than observing the emitted electrons, ultrafast X-ray or electron diffraction measures the diffraction patterns of incident X-rays (or electrons) as they interact with a molecule. Measuring this diffraction pattern at different points throughout a photochemical process can provide insights into how these aforementioned properties change as the molecule progresses through various excited states[6, 8, 9]. Time-resolved X-ray absorption spectroscopy can be used to determine the local structure of particular atoms at different points throughout an excitation. In brief, X-ray absorption spectroscopy measures the absorption of X-rays by the chosen molecule

as a function of X-ray energy. When the X-ray energy corresponds to the binding energy of a core electron in the molecule, that electron is excited and potentially ejected from the molecule, leading to an absorption feature that can inform as to the properties of the molecule. Tuning the X-ray energy to target specific absorption edges (corresponding to specific shells of a molecule, allows information about the target molecule’s electronic structure to be obtained)[7, 10, 11].

While the above techniques can provide a great wealth of information on a molecule’s nuclear and electronic structure, none of them are without their issues. Photoelectron spectroscopy relies on measurement of the electrons emitted by a molecule, rather than any measurement of the molecular products of the photochemical reaction themselves. X-ray and electron diffraction both suffer from less sensitivity towards light atoms, with smaller atoms possessing lower scattering cross-sections, and hence producing less clear diffraction patterns[12]. Finally X-ray absorption spectroscopy typically struggles to differentiate signals from atoms that lie close together in atomic number, with signals from Fe-C and Fe-N, for example, appearing similar in nature. Additionally, the absorption edge of the element of interest has to be within the energy range obtainable from the available experimental setup[11]. As there is currently no universal experimental imaging method that is perfectly suited to all reactions and molecules, having as wide a variety of methods in the experimentalist’s toolbox as possible is essential, so as to have alternatives when other methods encounter issues. As such, demonstrating that different techniques are applicable to as wide a variety of reaction dynamics as possible is important to establish novel methods as viable alternatives for when the situation requires them.

1.1.1 Coulomb Explosion Imaging

CEI is one such additional technique that should be considered when trying to study reaction dynamics. In simplest terms, CEI utilises the fact that like-charges Coulombically repel to fragment molecules, and then studies the momenta of the resultant fragments, as the fragment distribution corresponds to the molecular geometry at the time of explosion. CEI is accomplished using ultrafast high-intensity

laser pulses to remove electrons. Charges at different points on the molecule repel against each other, and result in the molecule splitting apart, producing two or more fragments with Coulombic momentum components. At the point of explosion, atomic motion is essentially ‘frozen’, and as such allows observation of the structure of the molecule at that point. While the concept of using molecular explosions as a method to determine structure is not novel (with early experimental work accelerating molecules to high-energy to strip electrons following their collision with a foil), multiple developments since the year 2000 have greatly expanded its capability as an imaging method[13]. The three most notable developments that enhance CEI are as follows: improvements in time-of-flight spectroscopy allow more accurate determination of fragment mass and initial velocity, allowing the disentanglement of fragments that possess similar mass-to-charge ratios that would have previously shown up as a single signal. Next, accurate position-sensitive detectors allow the positional information of any resultant fragments to be measured, which subsequently can lead to determination of the fragment geometry at the time of explosion. Finally the development of increasingly ultrafast lasers allow molecular ionisation prior to any significant nuclear motion occurring. Modern CEI utilises femtosecond laser pulses to image nuclear dynamics, and has shown promise as a method to complement the data extracted from the above previously mentioned techniques. Unlike X-ray/electron diffraction spectroscopy, CEI is equally sensitive to light and heavy atoms, and additionally directly measures the ionic products from a photochemical reaction[12]. Within this thesis, resultant fragments and charges are represented using A^{n+} notation, where A corresponds to the fragment and n to its charge. Figure 1.1 shows a schematic overview of the CEI process.

Depending on the type of laser inducing the charge, the charge can either be induced at multiple locations in the molecule simultaneously (if either multiple photons are absorbed by different atoms in the molecule, or tunnelling ionisation occurs), or only on one atom, where it subsequently redistributes around the remainder of the molecule. The former is more often seen in ionisation via an InfraRed (IR) pulse, whereas the latter is more prevalent with ionisation via an

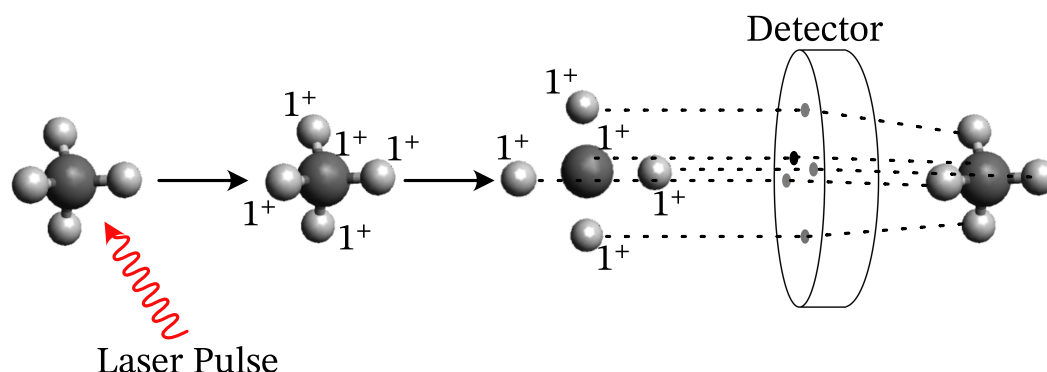


Figure 1.1: Schematic showing the principles behind Coulomb explosion imaging. First, a laser pulse induces multiple positive charges on the molecule. These charges repel, and result in the molecule fragmenting into multiple pieces. These fragments interact with a detector, and their arrival time and positional information are recorded. This temporal and positional information can then be used to determine the origin of each fragment, and hence the structure of the molecule prior to explosion.

eXtreme UltraViolet (XUV) or X-ray pulse. Both of these different ionisation regimes are expanded upon in Chapter 2. The greater the total charge state of the molecule, the greater the energy of the fragments, according to Coulomb’s law (Equation 1.1):

$$\sum_{j \neq i}^n \vec{F}_{ij} = \sum_{j \neq i}^n k \frac{q_i q_j}{r_{ij}}, \quad (1.1)$$

where q_i and q_j correspond to the fragment charges of fragments i and j respectively, r_{ij} is the separation of the two fragments, k is the Coulomb constant and corresponds to $8.987 \times 10^9 \text{ Nm}^2\text{C}^{-2}$ and F is the Coulombic force. Measurement of the energies and positions of these fragments relative to one another allows their locations at the time of explosion, and corresponding reaction channel of origin, to be determined.

Given that CEI has shown promise as a technique to study ultrafast chemical reactions, and also avoids some of the pitfalls of other existing techniques, demonstrating its suitability to follow a wide variety of different photochemical reactions, in a wide variety of different molecules, is essential to establish CEI as an additional tool for the characterisation of ultrafast photochemical reactions[13–17].

1.2 Outline of Thesis

This thesis builds upon prior time-resolved CEI studies[18–20], and provides evidence for CEI’s capability to characterise multiple different properties of molecular photodissociation dynamics, including, but not limited to, dissociation branching ratios and transient excited geometry changes. Here, the photodissociation pathways of three molecules were studied. The majority of the data was collected at Free Electron Laser (FEL) facilities, with some supporting data collected at the University of Oxford. The excitations were accomplished using UV pulses, and a variety of different pulses from the X-ray to IR regimes were used to induce Coulomb explosions.

A chapter-by-chapter outline is as follows: Chapter 2 details any underlying theory that is relevant to understanding the chemistry of the later chapters. This includes, but is not limited to, areas such as ionisation methods, pump-probe spectroscopy, and photoexcitation. Theory is only included in this chapter if it is applicable to multiple subsequent chapters - any background theory relating to the specific molecules will be discussed in that molecule’s own chapter. Chapter 3 is similar to Chapter 2, in that it focuses on any experimental instruments, techniques, data processing or analytical methods that are relevant to multiple subsequent chapters.

The data obtained in Chapters 4-6 looks at the photodissociations of specific molecules. The pump-probe study of CH_2BrI in Chapter 4 was used to show that CEI is capable of characterising many-body dissociation reactions. Chapter 5 uses CEI to determine the branching ratio, onset times, internal energy depositions and excited states of two independent dissociation mechanisms of iodobenzene. Chapter 6 looks at the photodissociation dynamics of CS_2 , and shows that CEI is sensitive to short lived transient excited states that include a structural change from a linear to bent geometry. For all of the above molecules, previous theoretical and experimental studies exist, allowing validation of the accuracy of the conclusions determined using the CEI data, and confirming its suitability for novel studies of molecules in the future.

Finally Chapter 7 provides a summary of the discoveries made in the thesis, such as how it has successfully been demonstrated that CEI is sensitive to ultrafast structural geometry changes across an excited state, how it can be used to characterise overlapping dissociation mechanisms and how through comparison to simple models the excited state of a fragment can be determined. Additionally, a brief example of ongoing developments that will advance the field of time-resolved CEI is provided.

1.3 Authorship Statement

Chapter 4 is based on work published in the paper: ‘Characterizing the multi-dimensional reaction dynamics of dihalomethanes using XUV-induced Coulomb explosion imaging’ by Walmsley, Unwin *et al.*, *Journal of Chemical Physics*, **159**, 144302 (2023). This paper additionally includes analysis of the photodissociation dynamics of CH₂I₂, explored by T. Walmsley. I would like to thank all the people involved in every part of this experiment, with contributions being made to the data collection at FLASH, discussion of the results, and feedback on the publication by: T. Walmsley, F. Allum, S. Bari, R. Boll, K. Borne, M. Brouard, P. Bucksbaum, N. Ekanayake, B. Erk, R. Forbes, A. J. Howard, P. Eng-Johnsson, J. W. L. Lee, Z. Liu, B. Manschwetus, R. Mason, C. Passow, J. Peschel, D. Rivas, D. Rolles, A. Rörig, A. Rouzée, C. Vallance, F. Ziaee, and M. Burt.

Chapter 5 is based on work submitted for publication in ACS Physical Chemistry AU in the paper: ‘Time-resolved probing of the iodobenzene C-band using XUV-induced electron transfer dynamics’ by Unwin *et al.* I would like to thank all the people involved in every part of this experiment, with contributions being made to the data collection at SACLA, discussion of the results, and feedback on the publication by: W. Razmus, F. Allum, M. Britton, M. Brouard, P. Bucksbaum, R. Forbes, M. Fushitani, I. Gabalski, T. Gejo, J. Harries, P. Hockett, A. J. Howard, H. Iwayama, E. Kukk, Y. Kumagi, C. Lam, J. McManus, R.S. Minns, K. Nagaya, A. Niozu, J. Niskanen, S. Owada, J. Pickering, D. Rolles, J. Somper, K. Ueda, S. Wada, T. Walmsley, J. Woodhouse, M. Burt, and E. M. Warne.

Chapter 6 is based on work published in the paper: ‘X-ray induced Coulomb explosion imaging of transient excited-state structural rearrangements in CS₂’ by Unwin *et al.*, *Communications Physics*, **6**, 309 (2023). I would like to thank all the people involved in every part of this experiment, with contributions being made to the data collection at FLASH, discussion of the results, and feedback on the publication by: F. Allum, M. Britton, I. Gabalski, H. Bromberger, M. Brouard, P. H. Bucksbaum, T. Driver, N. Ekanayake, D. Garg, E. Gougoula, D. Heathcote, A. J. Howard, P. Hockett, D. M. P. Holland, S. Kumar, C. Lam, J. W. L. Lee, J. McManus, J. Mikosch, D. Milesevic, R. S. Minns, C. C. Papadopoulou, C. Passow, W. O. Razmus, A. Röder, A. Rouzee, M. Schuurman, A. Simao, A. Stolow, A. Noor, C. Vallance, T. Walmsley, D. Rolles, B. Erk, M. Burt, and R. Forbes.

2

Theory

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This Chapter provides details of any general theory that is applicable throughout this thesis. Theory and previous work relating to a specific molecule shall be discussed in the associated data Chapter. An outline of this Chapter is as follows: firstly, an overview of the different ionisation regimes that were used to induce Coulomb explosions is provided. This is followed by an explanation of how introducing a time-dependence to a Coulomb explosion allows ultrafast dynamics to be studied. Next, an overview of the photochemical dynamics that are the target of analysis is given. Finally how electron migration between fragments can be used to determine dynamics is explored.

2.1 Ionisation Methods

Multiple different laser sources can Coulomb explode molecules, with wavelengths corresponding to the IR, XUV and soft X-ray regimes. These different wavelengths are achievable in different experimental instruments, and the sources of each are expanded upon in Chapter 3, but typically, IR wavelengths can be produced at smaller in-house experimental setups, while high-intensity XUV and X-ray pulses require larger, dedicated facilities (FELs). As mentioned in Chapter 1, the type of laser that ionises a molecule can affect how the multiple charges required for a Coulomb explosion are generated, with either multiple charges being induced on different atoms simultaneously, or alternatively, a high charge being induced on a single atom that subsequently redistributes around the molecule. Both of these processes are shown schematically in Figure 2.1.

The choice of ionisation pulse can also in some instances affect the observed fragmentations (due to the different mechanisms of achieving a high charge state), and hence complicate the observed reaction dynamics, and these effects should be considered when choosing an ionisation pulse[13–17].

Two primary methods of ionisation were used in this thesis to achieve the multiple positive charges necessary to induce Coulomb explosions and produce fragment ions: strong-field (which corresponds to using a high-intensity oscillating laser pulse) ionisation and core-hole ionisation. The employed method of ionisation is dependent on the power, wavelength and intensity of the utilised laser.

2.1.1 Strong-Field Ionisation

Smaller table-top laser setups typically ionise via longer wavelength pulses in the IR or Near-InfraRed (NIR) region (in the setup used for the data in this thesis, ionisation is achieved using an 800 nm pulse). These IR lasers produce highly charged molecules that undergo Coulomb explosions through strong-field ionisation. Strong-field ionisation occurs when the oscillating laser field is sufficiently intense to distort the potential barrier of the electron, and allow one or more valence electrons to escape the molecule, leaving a net positive charge.

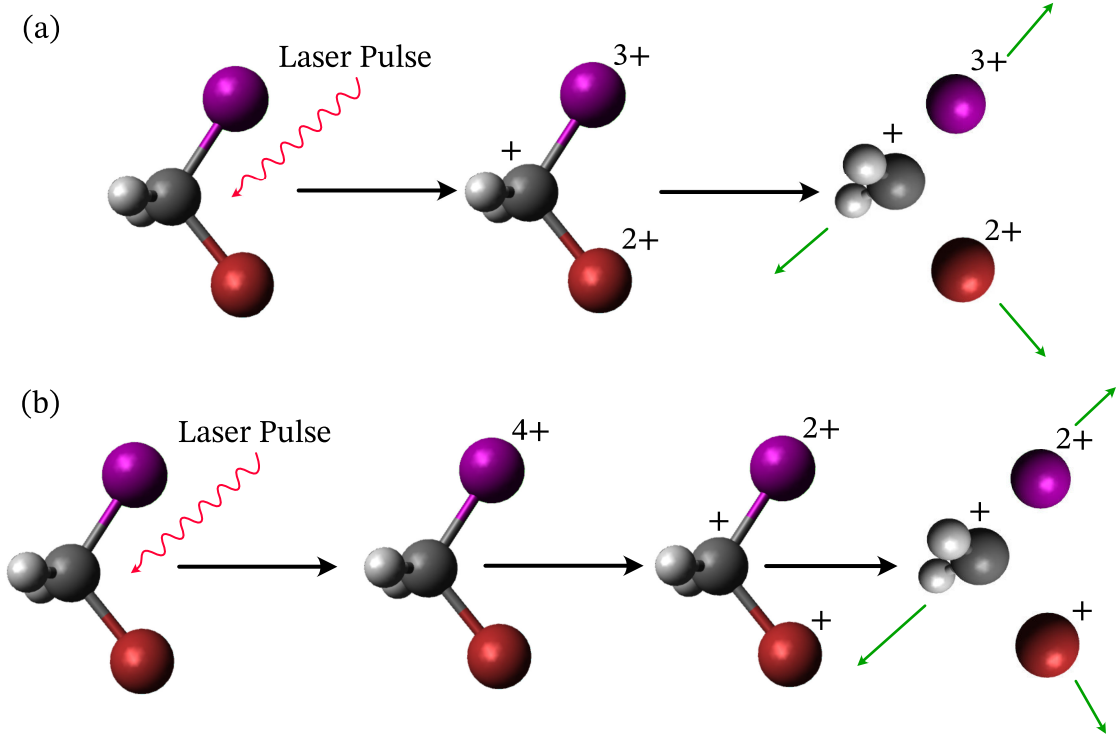


Figure 2.1: The two different mechanisms by which a Coulomb explosion can be induced. Panel (a) corresponds to where the laser pulse is able to ionise multiple atoms in a molecule simultaneously (in this case a bromine, carbon and iodine atom), and so these charges can directly repel and explode. Panel (b) corresponds to a single photon highly ionising a single atom (in this case iodine), with the charge later redistributing to elsewhere in the molecule followed by explosion. Green arrows correspond to recoil direction of fragments. Grey = carbon, purple = iodine and brown = bromine.

For an electron located in a potential well, the edge of this well can be distorted to varying degrees by its interaction with an intense laser field, and therefore the degree of this distortion is dependent on field intensity. The Keldysh parameter, γ , can be used to approximately identify the ionisation mechanism (accepting that there is likely some regime overlap close to the cross-over points). The Keldysh parameter is related to the ratio of an electron's ionisation potential (IP), and the energy of the laser. It is determined as shown below in Equation 2.1.

$$\gamma = \sqrt{\frac{I_p}{\frac{2E}{4\omega_0^2}}}, \quad (2.1)$$

where I_p is the molecule's ionisation energy, E is the laser electric field strength,

and ω_0 is the centre of the laser frequency. The effect on the potential barrier of a bound electron depending on different values of γ is shown in Figure 2.2. If $\gamma \ll 1$, then the potential barrier is somewhat distorted, as electrostatic repulsion forces the valence electrons away from the laser pulse. The potential barrier is dropped to an energy level where the electron is still trapped and cannot freely leave. Instead, the barrier is low enough that the electron is capable of tunnelling through, escaping the molecule and inducing a positive charge. If $\gamma \gg 1$, then the potential barrier is insufficiently distorted for tunnelling ionisation to occur. However, if the single photon is high enough in energy (or if multiphoton regimes occur), then enough energy can be imparted to the electron that it can escape above the potential barrier (known as Over-The-Barrier Ionisation (OTBI)). The intensity of the laser consequently also determines how many positive charges are produced, with greater intensities allowing more electrons to be lost[21, 22]. After the electron has been removed by the strong laser field, it is considered to be a free particle (Strong-Field Approximation (SFA)). This allows any interactions between the emitted electron and the parent molecule to be ignored, with dynamics being solely affected by the laser field, which simplifies the calculation of properties such as ionisation rate and electron momentum distributions. As stated, thanks to the SFA, interactions between the electron and parent molecule do not need to be considered. However, should the laser field reverse direction the free electron can be redirected back towards the parent molecule, where the electron's interaction with the parent molecule can lead to high-harmonic generation[23, 24].

One potential negative of strong-field ionisation is it typically happens sequentially, with electrons being removed one after another, as opposed to near-simultaneously. This can in some instances lead to nuclear motion within the pulse duration of the laser, but prior to Coulomb explosion. While there will always be some small motion within the duration of the laser (as a consequence of vibrational motion and a non-infinitely short pulse length), a slow charging-up time can result in ultrafast dynamics occurring within this time-period. This can

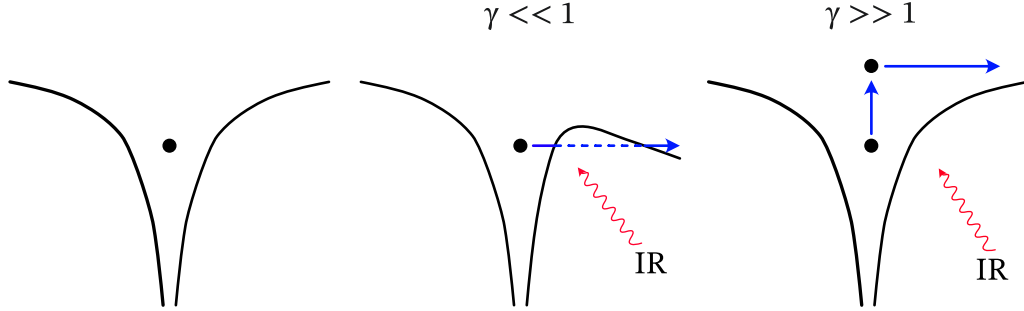


Figure 2.2: Schematic showing an electron bound in a potential well. Three situations are demonstrated: the electron bound without any interaction with a laser pulse, the electron when in contact with an IR pulse that induces tunnelling ionisation, and the electron when in contact with an IR pulse that induces OTBI/multi-photon ionisation.

result in explosion occurring from a combination of different charge states, and complicate analysis of the resultant dynamics[15, 25, 26].

2.1.2 Core-Hole Ionisation

An alternative method to achieve high charge states is core-hole ionisation followed by Auger-Meitner decay. Ionisation in this way achieves rapid and efficient charge build-up, leading to Coulomb explosion.

The continued development of FELs has allowed increasingly short pulse durations and high photon energies, and hence increasingly high intensity laser pulses, to be obtained. The tunability of these pulse energies, a key feature of FELs, enables the removal of core electrons from molecules as opposed to valence electrons. An additional benefit of these high intensity pulses is that their energies can be tuned to ionise just above a particular absorption band, and therefore allow some selectivity to which core electrons are removed[12, 27, 28].

While initially removing a core electron leads to only a single positive charge, a subsequent process known as an Auger-Meitner decay results in the rapid removal of additional electrons. This effect starts with an incident X-ray or XUV pulse ionising the parent molecule by removing a core electron. This leaves an empty hole in a core orbital, which is rapidly filled by the decay of an electron from a higher orbital into this inner-shell vacancy. The decay of this electron from

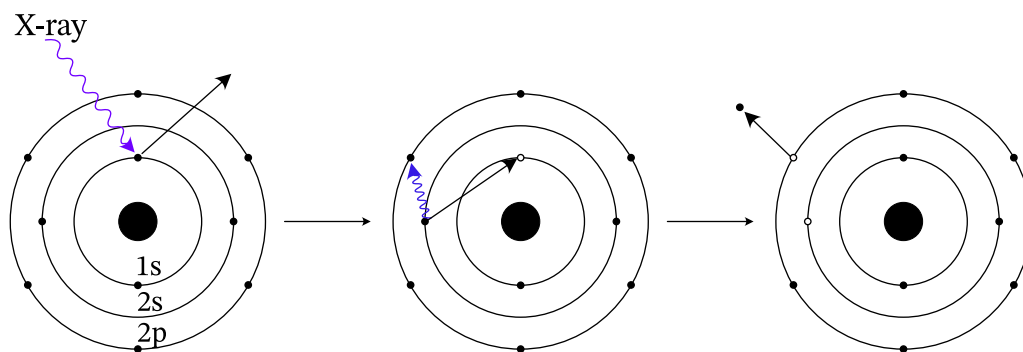


Figure 2.3: Schematic showing how multiple electrons can be removed from an atomic site of a molecule by X-ray core ionisation followed by Auger-Meitner decay.

a higher to lower orbital results in the release of energy. This energy can then interact with one or more higher shell electrons, causing them to be released from the atom, and hence induce multiple positive charges[29]. Charge build-up via core-hole ionisation can occur over a different time-scale to strong-field ionisation, and therefore can potentially help avoid dynamics during the charging-up process[30, 31]. Figure 2.3 shows the three steps described above of X-ray ionisation, Auger decay, and finally emission of an Auger electron. This high charge state on the ionised atom can then redistribute around the rest of the molecule to induce a Coulomb explosion as shown in Figure 2.1.

2.2 Pump-Probe Spectroscopy

Using a single pulse to induce a Coulomb explosion, as described in Section 1.1.1, is helpful for studying time-independent molecular properties[32]. However, as explained above, when the molecule is exploded by the laser pulse, the fragment distribution corresponds to the molecular geometry at the time of explosion. This allows CEI's capabilities to be enhanced by introducing a time-dependence to the experiment and exploding the molecule at different instances over the course of a chemical reaction. This can be used to follow ultrafast reaction dynamics, such as the photodissociation reactions examined within this thesis[33].

This time-dependent CEI is a form of pump-probe spectroscopy. Pump-probe spectroscopy can be used to study reaction dynamics on ultrafast timescales. It

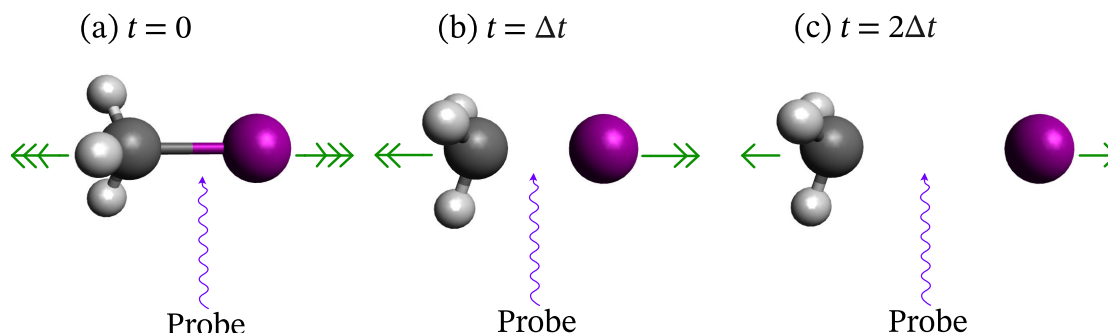


Figure 2.4: Cartoon representation of how varying the delay time between the two laser pulses enables a molecule to be studied throughout a photochemical process. In each of the three panels (a)-(c) the ground state molecule is excited by a UV pump pulse, initiating a dissociation. (a) shows the effect of probing the molecule at $t=0$, i.e. when the probe pulse arrives at the same time as the UV pulse. (b) shows the effect of probing at $t=\Delta t$, where the bond has dissociated, and (c) shows the effect of probing at $t=2\Delta t$, where the bond has dissociated, and the resulting fragments have an increased separation. In each case the measured observable after interaction with the probe pulse will be different, and hence the molecular dynamics of this dissociation can be followed. The shorter the separation of the fragments, the greater the Coulombic repulsion after ionisation, and so the greater the momenta of the fragments (indicated here by green arrows).

requires two laser pulses - a ‘pump’ pulse and a ‘probe’ pulse. The pump pulse initiates some photochemical reaction (such as a dissociation or isomerisation), and then the probe pulse interacts with the molecule in a measurable way (such as by detecting a changing absorption profile). As the probe pulse observes the structure of the molecule at their interaction time, by changing the delay period between the two laser pulses, the evolution of a molecule along a reaction coordinate can be studied. The increased time separation between the two pulses allows more time for the molecule to travel along a potential energy surface, and therefore the measured observable will be different. In this thesis the pump pulse is always a UV wavelength, while the probe pulse varies from a soft X-ray to an IR pulse, and is used to induce a Coulomb explosion in the excited molecule. This pump-probe explanation is shown in cartoon form in Figure 2.4, where at shorter delay times the induced charges on the fragment are closer together, resulting in greater Coulombic repulsion compared to longer delays[34, 35].

2.3 Photoexcitation and Photodissociation

The dynamics of interest that will be explored throughout this thesis are photodissociation reactions. After interaction of a molecule with light, the majority of systems have multiple excited states that are accessible, that is, states with more energy than the ground state minimum. One such way that these higher energy states can be accessed is by the absorption of photons, which impart energy into the molecule, and induce an electronic transition to an electronically excited state. Therefore, the number of accessible excited states is dependent on the energy of the supplied photon, with a higher energy photon allowing access to additional and higher energy states.

For each of these excited states, a molecule can have any number of combinations of bond lengths, angles, and electronic arrangements. The energy of these combinations can be represented by a Potential Energy Surface (PES), with different configurations giving different energies. Therefore, a PES shows how the energy of a state changes with the varying of each of these possible parameters. Figure 2.5 shows example Potential Energy Curves (PECs), which correspond to a 2D slice of a multidimensional PES, in this case looking at selected excited states for CH_2I_2 . For each curve, the energy of the excited states are shown as a function of I-C-I bond angle between 80° - 120° , for different fixed C-I bond lengths, ranging from 2.1 to 2.4 Å. These PECs were simulated using unrestricted b3lyp density functional theory with a def2tzvp basis set by Z. Liu, and are intended to demonstrate how the energies of each state varies with changing geometries. Each of the PECs in Figure 2.5 can be seen to have a point of minimum energy, and it is apparent that this minimum energy point shifts as the structural parameters of the molecule are changed. A system always wants to go towards its energy minimum configuration, and so this explains why molecules undergo a structural rearrangement after excitation. If excitation occurs from one state to another, while a molecule may lie at the energy minimum on the ground state, the corresponding point on an excited state may not. As such, the properties of the molecule will shift to readopt the position on the PES with the lowest energy. Additionally, locations

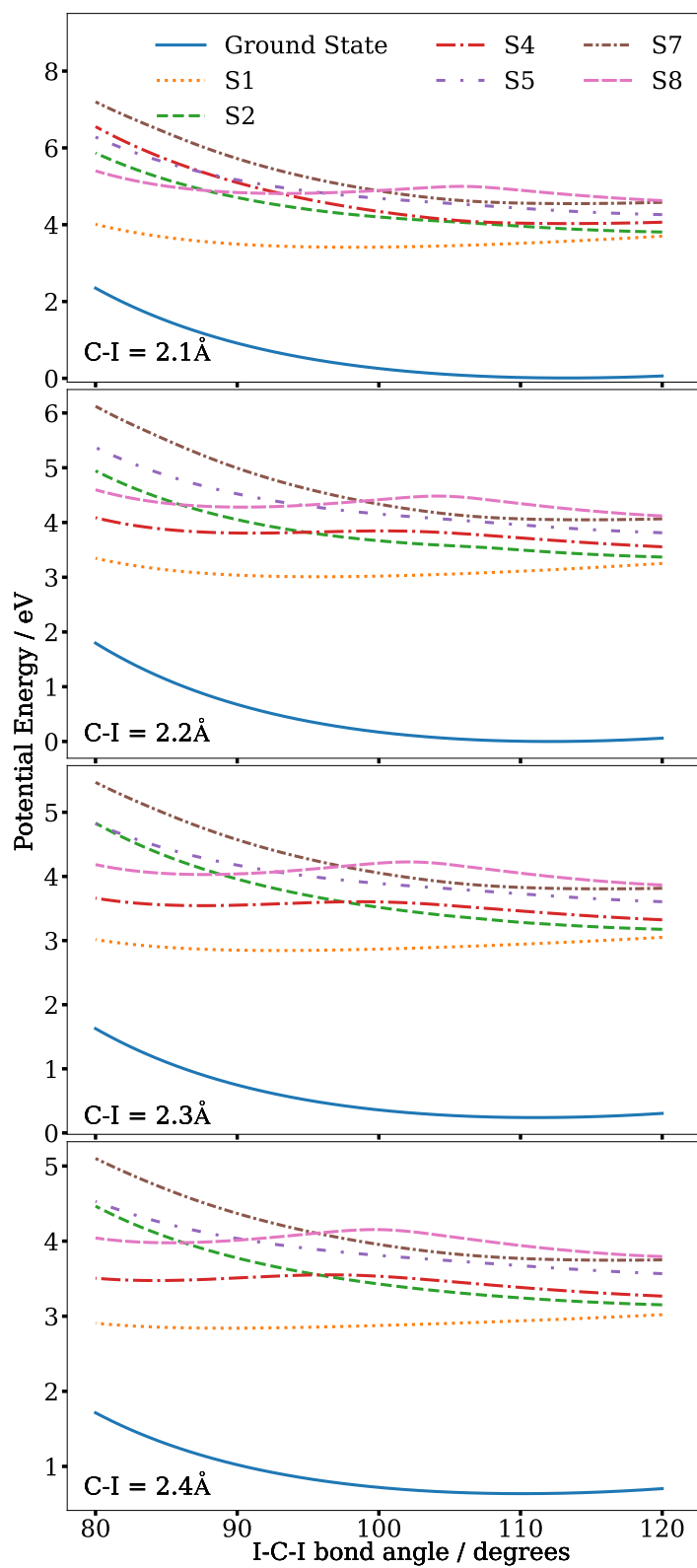


Figure 2.5: Simulated PECs for CH_2I_2 plotted as energy as a function of I-C-I bond angle between 80 and 120° for different C-I bond lengths. It can be seen that the energy minimum of each state varies as the bond length and bond angle is changed. Simulated by Z. Liu using unrestricted b3lyp density functional theory with a def2tzvp basis set.

where different curves touch or overlap can help facilitate migration between states, and this shall be expanded upon further below.

Upon excitation to an excited state multiple different electronic transitions can occur, leading to the molecule either progressing to different vibrational levels within an excited state via vibrational relaxation, or transitioning to a different PES via either internal conversion or intersystem crossing. Both internal conversion and intersystem crossing result in a change of adopted excited state, and both are non-radiative transitions. Selection rules govern whether a particular transition is allowed or forbidden, and therefore whether a transition is likely or unlikely to occur. The Spin Selection Rule states that transitions between states with different spin multiplicity are forbidden, while the Laporte Selection Rule prevents transitions between states with the same symmetry with respect to an inversion centre. Internal conversion corresponds to a spin-allowed transition, i.e. where no change in electron spin occurs during the transition, and therefore occurs rapidly. Conversely, during intersystem crossing the spin of an electron changes, and therefore is typically spin-forbidden, however spin-orbit coupling (the interaction between an electron's spin and its orbital motion) allows it to be weakly permitted, albeit on a considerably longer timescale than spin-allowed transitions. These transitions between excited states and vibrational energy levels can be simply represented in a Jablonski diagram, as shown in Figure 2.6.

Given that PESs can have different energy maxima and minima from neighbouring excited states, in some instances the PESs of two or more adjacent surfaces possess regions of degeneracy, where they touch or overlap. These regions of degeneracy can form a conical intersection which encourages migration from one excited state to another via internal conversion. Additionally, in some instances intersystem crossing can occur more rapidly between states with similar energies[36–39].

Photoexcitation can subsequently lead to dissociation, that is, the cleaving of one or more molecular bonds, if the excited state is repulsive, dissociative or unbound. The likelihood of this occurring depends on the energy of the excitation photon, and the nature of the available excited states. Should the molecule be excited to an

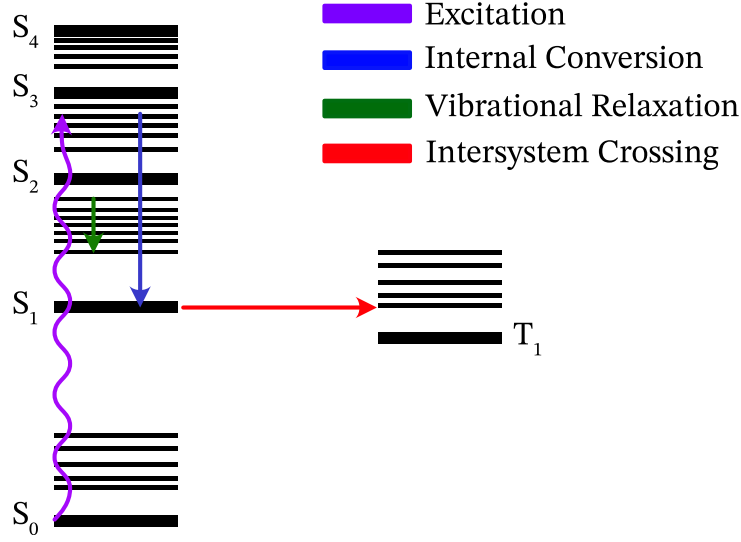
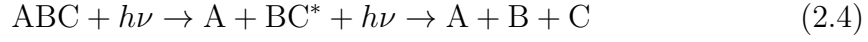


Figure 2.6: Jablonski diagram showing multiple different non-radiative transitions that can occur between different excited states.

unbound excited state (or be excited to a state that lies in close enough proximity to an unbound state that is accessible by internal conversion or intersystem crossing), a bond can break, leading to two photoproducts (Equation 2.2). This dissociation can occur rapidly after excitation should quick progression to the dissociative state occur, or if the molecule is excited to the dissociative state directly. Alternatively, it can occur on a slower timescale, should excitation lead to a predissociative state, where notable structural changes can occur, prior to dissociation. If the excitation photon is sufficiently high in energy (or multiple low energy photons are absorbed), and depending on the bond dissociation energies of the molecule (D_0), additional dissociations can occur after the first bond cleavage in either a concerted or sequential manner (Equations 2.3 and 2.4)[40, 41].





2.4 Born-Oppenheimer Approximation

The calculation of the above described potential energy surfaces relies on the Born-Oppenheimer approximation to dramatically shorten and simplify the computational processes. Equation 2.5 shows how the Hamiltonian of a system can be written as a sum of the Coulombic interactions of the nuclei and electrons (V), as well as their respective kinetic energies (T), where e and n correspond to electrons and nuclei respectively.

$$\hat{H} = \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn} + \hat{T}_e + \hat{T}_n \quad (2.5)$$

The Born-Oppenheimer approximation assumes that, due to the large difference in mass of a nucleus and an electron, when considering electronic motion the nuclear velocity can be assumed to be zero, when compared to the much faster electrons (as within the time-period of an electron, the nucleus will have essentially remained stationary).

Given that the solely nuclear contributions can now be considered to be zero, the full Hamiltonian can be reduced to the electronic Hamiltonian ($\hat{H}_e$), and this is given by Equation 2.6.

$$\hat{H}_e = \hat{V}_{ee} + \hat{V}_{en} + \hat{T}_e \quad (2.6)$$

Again, by considering the nuclei as fixed rather than motile the time-independent Schrödinger equation can be given as the electronic Schrödinger equation (which again removes any variable nuclear components that would exist if the nuclear contributions were not assumed to be zero), as seen in Equation 2.7:

$$\hat{H}_e(r, R)\psi_e(r, R) = E_e(R)\psi_e(r, R), \quad (2.7)$$

where r and R correspond to the positions of the electrons and nuclei, $\psi_e(\hat{r}, R)$ corresponds to the vibronic wavefunction, and E_e corresponds to the electronic eigenvalues. Given that the nuclear velocities are zero according to the Born-Oppenheimer approximation, R can be considered fixed. Therefore, for the fixed values of R , E_e can be calculated for those chosen values, and this eigenvalue corresponds to the potential energy for this configuration of nuclear coordinates. R can then be varied, and for each combination of nuclear coordinates, a different electronic eigenvalue calculated. The result of this is a set of eigenvalues each corresponding to a particular nuclear configuration, or in other words, a PES.

It should be remembered that while the Born-Oppenheimer approximation can be considered accurate for many excited systems, in cases where the PESs are close in energy and touch (i.e. in the aforementioned conical intersections), the approximation breaks down. It is this break down, and therefore the coupling of the electronic and vibrational wavefunctions, that permits electrons to migrate from one state to another. An example of this will be seen in Chapter 6, where the electrons in excited CS₂ migrate through a conical intersection to a dissociated state[42–44].

2.5 Charge Transfer and the Over the Barrier Model

Charge Transfer (CT) is the process whereby an electron can migrate from a neutral fragment to help stabilise a positive charge on a more highly charged ion. This process has a distance dependence, with increasing separation of the charged and neutral fragments leading to a decrease in the likelihood of charge transfer occurring. This is due to an increase in the classical potential barrier for electron migration between the two fragments. At a certain distance the potential barrier is greater than the binding energy of the electron, and charge transfer is unable to occur. This fragment separation is known as the ‘critical distance’ (R_{crit}). Therefore, in practice there are three different events that can occur depending on fragment separation, as shown in Figure 2.7[45–47].

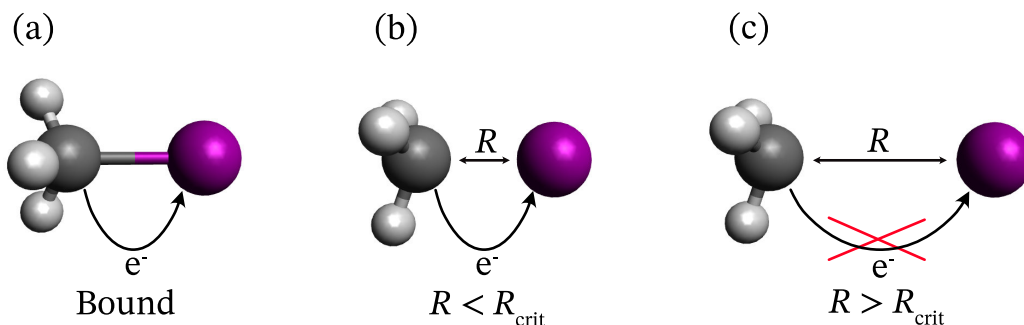


Figure 2.7: Possible electron transfer processes that can or cannot occur depending on fragment separation, R .

These possible pathways are: firstly at short separations while the fragments are still bound, electrons can move to different locations in the molecule (Figure 2.7(a)). Secondly, after dissociation, if the fragments are at a separation less than R_{crit} , then, similar to Figure 2.7(a), an electron can migrate from the neutral fragment to stabilise the positive charge (Figure 2.7(b)), and the fragments exist as $A^{(n-1)+}$ and B^+ . Finally, at separations greater than R_{crit} , the potential barrier for charge transfer is too great, and the fragments remain as A^{n+} and B (Figure 2.7(c)). As CT has a distance dependence for molecules undergoing a dissociation, it also possesses a time dependence due to the velocities imparted to the dissociated fragments. Prior to dissociation, and at short delay times after dissociation, the separation of the two fragments is small, and hence R is less than R_{crit} , and an electron can migrate, meaning there are two charged fragments that Coulombically repel with high momenta (Figure 2.7(a) and (b)). At larger delay times, the separation of the fragments is large, and R is greater than R_{crit} . At this separation CT can no longer occur, and there is no second charged species for the highly charged ion to repel against, resulting in fragments possessing only energy remaining from the dissociation (Figure 2.7(c)). For ions of the same atom, but with different charge states, R_{crit} (and consequently the critical time, t_{crit}) increases with increasing charge state, due to an increasing attraction on the electron. This increasing time is shown for experimental data in Figure 2.8 for $\text{I}^{2/3/4+}$ and allows information about the dissociation to be extracted.

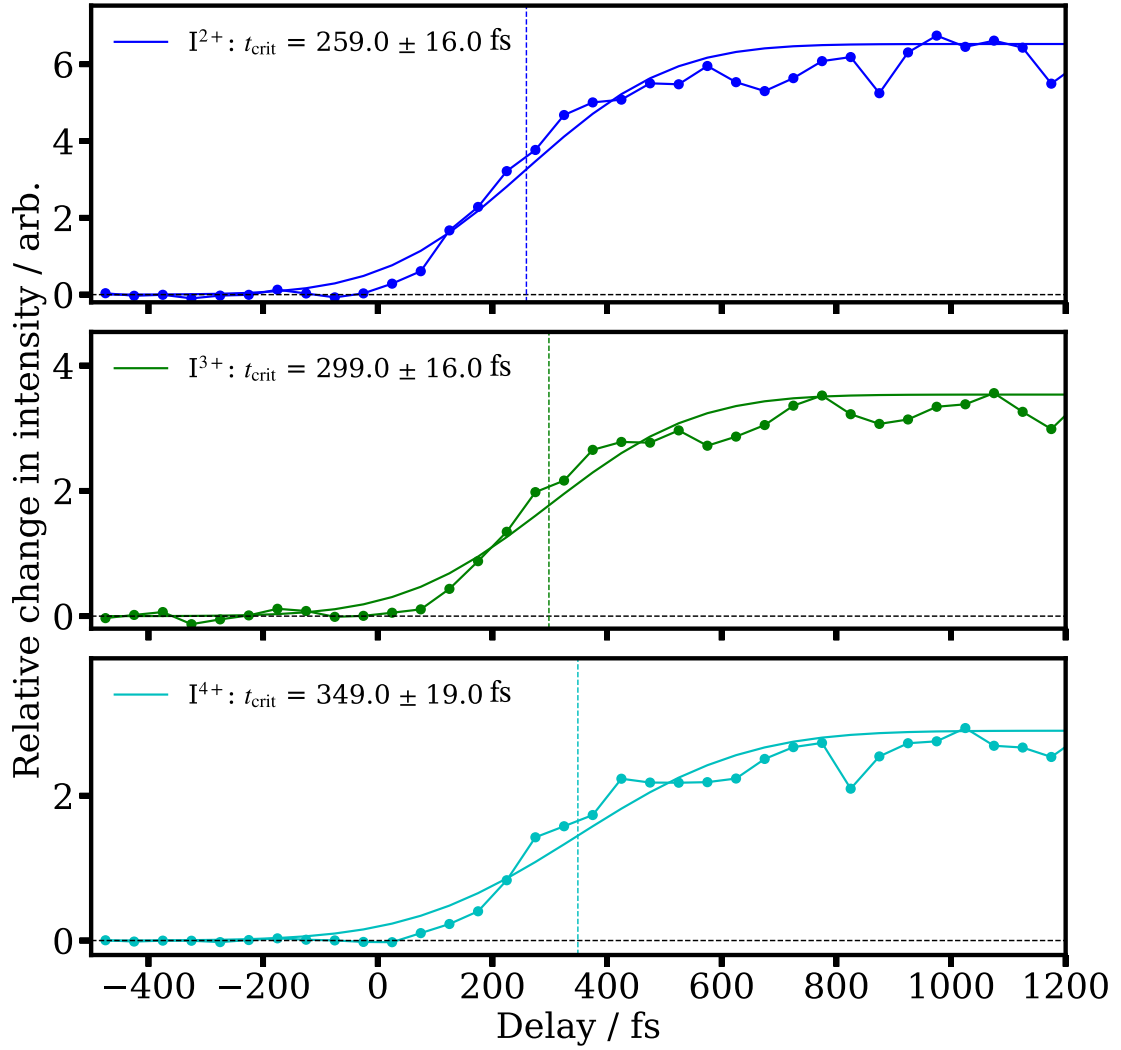


Figure 2.8: Increasing t_{crit} values for $\text{I}^{2/3/4+}$ from the photodissociation of CH_2BrI . Obtained by fitting a cumulative distribution function to the low momentum channel. Full dataset presented and explored in Chapter 4.

As mentioned above, information about the dissociation can be extracted by looking at the distance dependence of the CT process in different ion charge states. Comparison of either the experimental R_{crit} or t_{crit} to that which can be predicted by a classical Coulombic over-the-barrier (OTB) model, can help identify which fragments exist post-dissociation, and hence the nature of the dissociation. The OTB model is a ballistic model, and predicts the R_{crit} value for two fragments and is only dependent on the charge on the electron acceptor, and the ionisation potential of the donating fragment, as seen in Equation 2.8:

$$R_{\text{crit}} = ke^2 \times \frac{1 + 2\sqrt{n}}{\text{IP}}, \quad (2.8)$$

where k is the Coulomb constant, e is the charge on an electron, n is the charge integer, and IP is the electron donator ionisation potential. If strong agreement is found between the experimental and OTB values of R_{crit} for multiple different electron-accepting ion charge states, then the chosen electron donator is likely a product of the dissociation. If strong disagreement is seen, then either the electron donator is not a product of the dissociation or the dissociation is not ballistic, due to a molecular centre of mass that doesn't lie along the bond-vector[20, 48–50]. Comparison of the experimental data to the OTB model will be used in subsequent chapters to determine both that a dissociation occurs via a three- rather than two-body mechanism, and also to identify the excited state of the cofragment to a dissociation.

2.6 Summary

This Chapter has provided details of theory relating to the mechanism used to study dynamics, the dynamics studied within this thesis, and how interactions between the fragments can be used to deduce the nature of the dynamics. As mentioned at the start of this Chapter, any theory relating to the dynamics of the individual molecules that are studied throughout this thesis will be given in the relevant data chapters.

3

Experimental and Analytical Methods

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Similar to Chapter 2, any experimental instruments, techniques or analytical methods that apply generally to the entire thesis, or that are utilised in the study of multiple different molecules, are discussed here. Exact details of the experimental setups used for collecting each data-set, as well as any analysis methods only used for single molecules, are discussed in the Chapter associated with that molecule. This Chapter is structured in such a way as to guide the reader through the different instruments involved in the different steps of collecting data via a CEI

experiment. This process can be subdivided into four main sections: ion generation (Section 3.1), ion direction (Section 3.2), ion detection (Section 3.3) and data processing and analysis (Section 3.4).

3.1 Ion Generation

As explained in Section 2.2, studying time-resolved photochemical reactions via CEI requires a pump pulse to initiate the reaction, and a probe pulse to initiate the Coulomb explosion and allow it to be studied. This section examines the different types of laser systems used to initiate these processes.

3.1.1 Laser Systems

Two different types of laser were used to generate the probe pulses for data collection: FELs and a Ti:Sapphire laser system.

Free Electron Lasers

Two different FELs were used in this thesis: FLASH (the Free Electron LASer at Hamburg), was used to obtain the data shown in Chapters 4 & 6, while SACLA (the SPring-8 Angstrom Compact free electron LASer), produced the data in Chapter 5. One of the key advantages FELs provide over other laser systems, is that, as described in Section 2.1.2, the wavelength of the laser pulse can be tuned to ionise above a specific core orbital[51–53]. This site-selectivity of the probe energy makes it ideal to initiate Coulomb explosions, as the probe allows precise control over where the charge is placed in the molecule.

Both FLASH and SACLA are Self-Amplified Spontaneous Emission (SASE) FELs. All FELs have slightly different technical setups, and an overview of their general mechanism is described below. SASE FELs are able to produce high intensity XUV and X-ray pulses with radiation produced at the start of the beamline subsequently used as the seed for the desired pulse later in the beamline[54].

A typical SASE FEL comprises five different sections, shown schematically in Figure 3.1 for the FLASH2 beamline. Firstly, the system starts with an electron

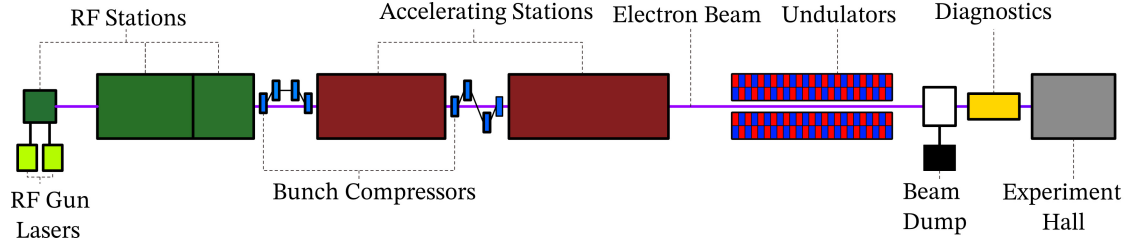


Figure 3.1: Simplified schematic of the experimental setup of the FLASH2 beamline located at the Free electron LASer at Hamburg facility. Recreated from Reference [53].

source, usually a RadioFrequency(RF)-gun-photoinjector. This RF-gun uses a short pulse duration laser to illuminate a photocathode in a microcavity, which releases the initial electrons into the beamline. After injection, the electrons enter multiple accelerating units, which rapidly increase the velocity of the source electrons. In between accelerating modules, bunch compressors help mitigate space-charge forces at low electron energy, and also any energy spread at higher energies. Following acceleration and compression, the desired experimental pulse is produced. This occurs in a section of the beamline called an undulator, consisting of a long setup of alternating magnets. When the accelerated electrons enter the undulator, the magnetic field causes them to oscillate laterally to the direction of the beamline, and emit incoherent radiation. This modulates the energy of the electron beam, causes some electrons to bunch and leads to coherent emission. The gradual increase in radiation intensity subsequently bunches all electrons and the final high-power, ultrashort XUV or X-ray pulse is produced. This fully bunched electron beam is directed down the beamline and used for experiments. The wavelength of the emitted radiation λ_e is given by Equation 3.1[52]

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

with λ_u being the undulator energy wavelength, γ is the Lorentz factor, and K is a measure of undulator strength, given by Equation 3.2

$$K = \frac{eB\lambda_u}{2\pi m_e c}, \quad (3.2)$$

where e is electron charge, B is peak magnetic field strength, m_e is the mass of an electron and c is the speed of light. Equations 3.1 and 3.2 show that by adjusting the strength of the magnetic field, or the wavelength of the undulator energy, it is possible to tune the emitted FEL radiation to a specific wavelength.

For details on the exact technical parameters of both the FLASH and SACLA FELs please see References [53] and [55] respectively. For a simplified overview of the experimental setup at the FLASH2 FEL beamline, see Figure 3.1.

Solstice Ace

The probe pulse used in the in-house University of Oxford experimental setup was an 800 nm IR pulse. This was generated by a Spectra-Physics Solstice Ace system. Figure 3.2 shows a simple schematic of the major steps involved in the generation of the IR probe pulse. Firstly, this system uses a Ti:Sapphire MaiTai Oscillator as a seed laser, which produces 800 nm pulses with a bandwidth of 60 nm at a frequency of 80 MHz. A four-level ND:YLF Diode-Pumped Solid State Ascend laser produces frequency doubled 527 nm pulses at a frequency of 1 kHz, and is used as a pump to amplify the MaiTai output. Amplification is performed via chirped-pulse amplification (CPA) in a regenerative amplifier (regen). CPA allows the short pulse to be amplified to high-intensities without damaging the optics within the regen. A brief summary of CPA within the regen is as follows: initially the short oscillator pulse is stretched in time. The amplification crystal is pumped with the laser pulse from the Ascend laser, and placed in an optical cavity, allowing the oscillator pulse to resonate through the pumped crystal multiple times and increase in energy. After the desired energy is achieved, the lengthened pulse is extracted from the crystal[56]. Finally, the uncompressed 800 nm pulse is passed through a compressor to produce compressed 800 nm pulses with a frequency of 1 kHz, bandwidth of 60 nm, pulse width of 35 fs and power of approximately 5 W. It is worth noting that these pulse measurements only apply at the source, and the intensity in the interaction region differs from these values due to power loss and pulse duration broadening resulting from optics along the beam path.

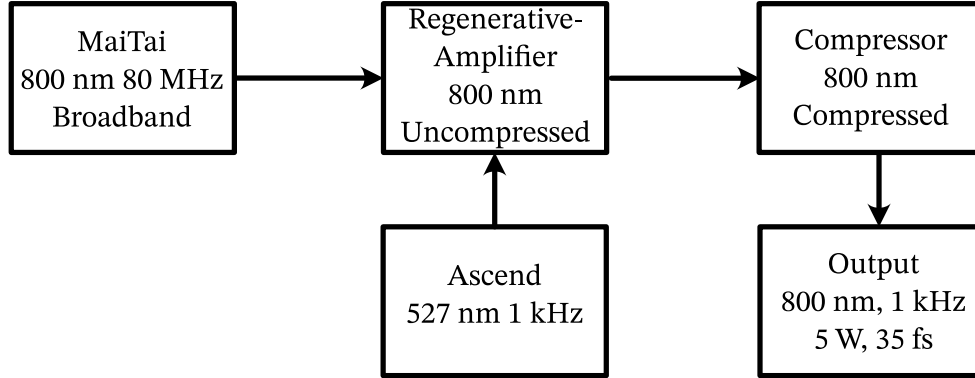


Figure 3.2: Simplified schematic showing the key steps in generation of the probe pulse used at the University of Oxford.

TOPAS Prime

The pump pulse used in the in-house University of Oxford experimental setup was a 200 nm UV pulse, produced by a Tuneable Optical Parametric Amplifier System (TOPAS) from Light Conversion. The TOPAS is powered using 70% of the output from the Solstice Ace system, therefore taking ~ 3.5 W of an 800 nm, 35 fs pulse as the pump laser. In the TOPAS, the pump pulse from the Solstice is overlapped with a white light signal pulse (which is also generated by the Solstice). Each pump pulse is converted into additional signal pulses and waste ‘idler’ pulses. The signal pulses produced from the pump are the same wavelength as the desired signal output, therefore allowing amplification of the output.

The photon energy of the idler pulses is equal to the difference between the pump and white light signal pulses, and these idler pulses are either discarded, or overlapped and mixed with the other pulses to produce a desired output wavelength. Using a white light source as the signal, rather than a single wavelength, enables a variety of output wavelengths to be obtained by tuning the chirp and phase matching of the white light and pump pulses. Wavelengths from 189-1600 nm are accessible with the TOPAS, when used with a Visible-Ultraviolet-Deep ultraviolet module. Shown in Figure 3.3 are the tuning curves for the TOPAS, which give

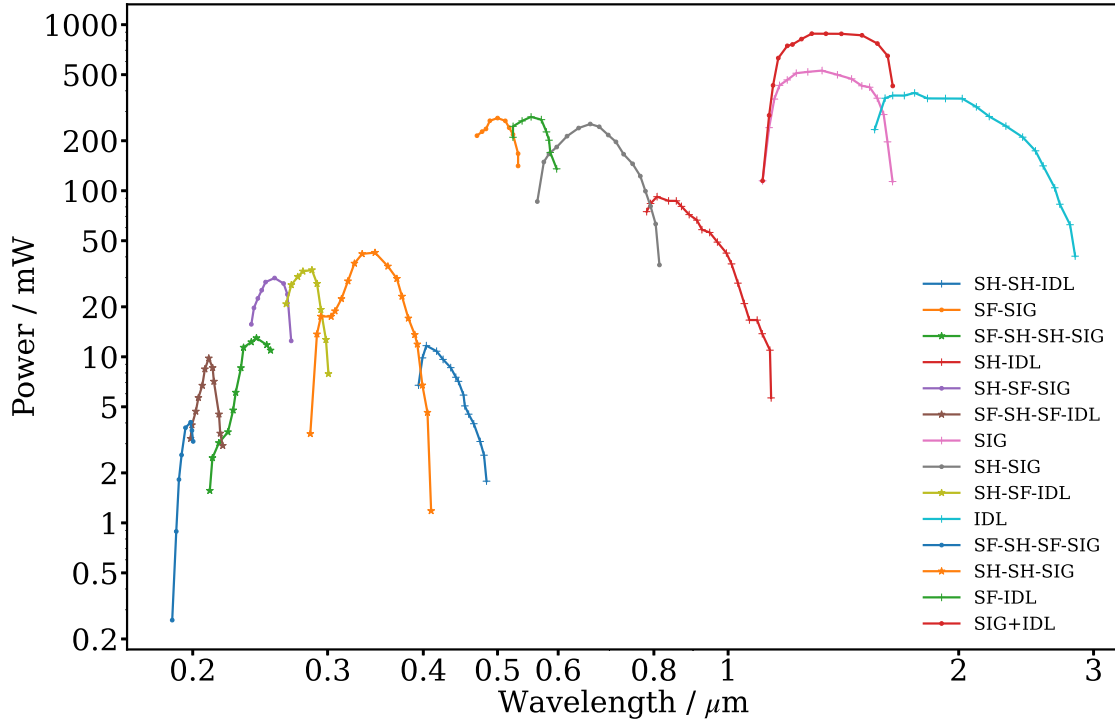


Figure 3.3: Achievable wavelengths in the TOPAS by the overlapping and non-linear mixing of different pulses. Used are the signal pulse (SIG), idler pulse (IDL) and second harmonic (SH) pulse. For cases involving sum frequency generation (SF), pulses are overlapped with the input pump pulse.

achievable wavelengths and approximate power output at each wavelength. Different wavelengths are achieved by the combination of different pulses within the TOPAS, which include SIGNAL (SIG), IDLER (IDL) and Second Harmonic (SH) pulses. Overlap with the input pump pulse also allows access to greater wavelengths via Sum Frequency generation (SF). At the used experimental wavelength of 200 nm, an average emitted power of 7 mW was recorded, although as above losses will occur along the beam path.

Figure 3.4 shows a schematic of the laser table setup utilised for the collection of the UV/IR data (using Solstice and TOPAS laser systems) in Chapter 5. Both pulses were directed around the laser table by optical mirrors, coated for specific wavelengths. A periscope system was used to adjust the UV pulse height to coincide with the IR pulse and a combining mirror was situated after both focusing lenses to overlap the two pulses. A computer-controlled Newport delay stage was placed in the IR beam path to allow the delay between the pump and probe pulses to be adjusted.

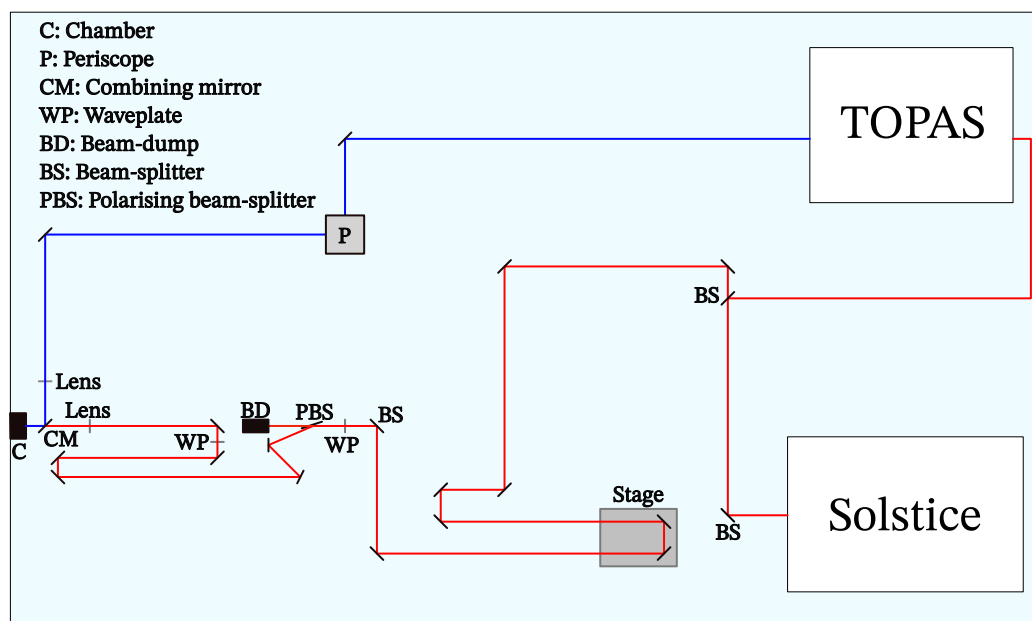


Figure 3.4: Schematic of the laser setup used to obtain the UV-pump, IR-probe data described in Chapter 5.

3.2 Ion Direction

After the molecule has undergone a Coulomb explosion, and exists as multiple charged fragments, a process called Velocity Map Imaging (VMI) is used to direct ions along the Time-of-Flight (ToF) tube[57].

3.2.1 Velocity Map Imaging

ToF mass spectrometry measures the yield of each type of ion species produced during an ionisation event. Supplementing ToF mass spectrometry with VMI allows extraction of additional information about formed ions, such as their momenta, and through subsequent analysis, their reaction channel of origin. In addition to obtaining the ToF spectrum of each ion, VMI is also able to measure a full velocity distribution, allowing different ions with the same m/z , or the same ion produced through two different reaction channels, to be distinguished, as ions produced during significantly different ionisation processes will likely have different momenta, despite having the same m/z .

A VMI spectrometer uses a minimum of four ion optics (each of which is an open plate capable of taking a variable voltage) to focus any ions produced along a ToF tube and onto a position sensitive detector. The ToF of an ion is given by Equation 3.3:

$$ToF \propto \sqrt{\frac{m}{zV_r}}, \quad (3.3)$$

where m corresponds to mass, z to charge and V_r is the voltage of the repeller ion optic. A four-plate VMI spectrometer setup used for CEI, comprising repeller, extractor, lens and ground plates is shown in Figure 3.5. The repeller and extractor plates direct all ions along the ToF tube, while the lens focuses the ions onto specific points on the detector. All ions with the same initial momenta are focused onto the same point on the detector, regardless of their location in the interaction region, enabling ions with the same m/z but produced from different events to be easily distinguished. The produced ions can have initial momentum either towards, or in the opposite direction of, the detector. This leads to the formation of a Newton Sphere, where ions that have initial momenta towards the detector are found at the front of the sphere, and ions with momenta opposite to the detector are found at the back, due to the slight time differences from the ions being redirected towards the detector by the ion optics. When the Newton sphere interacts with the detector, it is compressed down to a 2D image. Depending on the detector/camera combination used in acquiring data, the variation in arrival time for ions at the front and back of the Newton sphere can be measured[57–60].

In practice, focusing ions onto a detector with velocity mapping conditions results in regions of high and low activation on the detector, corresponding to the detector being illuminated if the induced Coulomb explosion produces fragments that map to a particular radius on the detector, or unlit for regions where no ion interacts. Lower momenta fragments are seen closer to the centre of the detector, while faster fragments are found nearer the edge as their higher momenta allows fragments to spread out a greater amount before colliding with the detector. Measurement of the radius from the centre of the detector the fragment appears

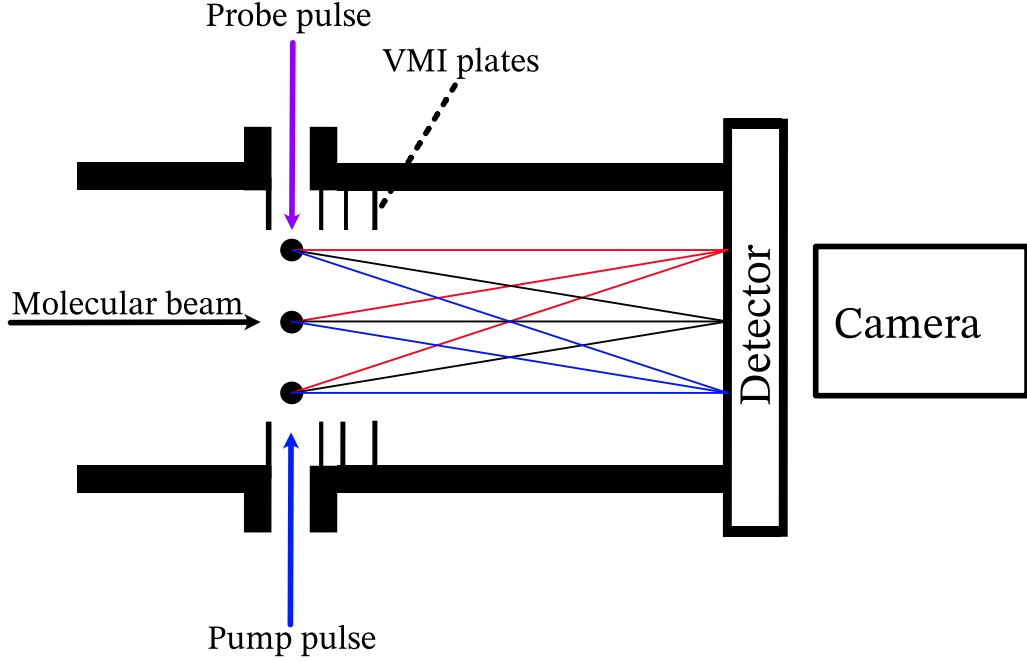


Figure 3.5: A schematic of a VMI setup used in a CEI pump-probe experiment. Three charged ion optics (repeller, extractor, and lens) are included, as well as a ground plate.

at allows the Kinetic Energy (KE) (and subsequently momentum) of the ion to be determined by Equation 3.4:

$$KE = \frac{1}{2}m\left[\frac{R}{Nt}\right]^2, \quad (3.4)$$

where m is mass, R is radius, t is ToF and N is a magnification factor which corresponds to actual versus expected image size on the detector[57].

Tuning of the ion optic voltages allows an experimental setup to be modified to better capture higher or lower velocity fragments, with higher ion optic voltages accelerating the fragments to the detector more quickly, and hence allowing less time for fast fragments to spread out. This consequently decreases the risk of them missing the edge of the detector. Conversely, utilising low ion optic voltages can enhance signal from low velocity fragments, as the signal will be spread over a wider radius on the detector. The resultant data can be filtered by ToF and plotted as ‘ion images’, which show detector hits for the chosen ions. Example ion images

are shown in Figure 3.6 for the production of I^{2+} and C_6H_2^+ from the Coulomb explosion of iodobenzene. There is a large difference in the appearance of these two ion images, with multiple features visible in C_6H_2^+ (a ring and a high intensity central region), while the central region dominates in I^{2+} . The different locations on the detector the features appear at are indicative of their different dynamics and momenta, with a greater radius from the centre of the detector corresponding to a fragment possessing a higher momentum. Multiple regions of high intensity usually indicate multiple different reaction channels producing fragments of the same ion but with different momenta (although it can on occasion be the result of two ions with the same m/z)[57].

3.3 Ion Detection

After the ions are directed along the ToF tube by the VMI optics, they are recorded by a detector. Depending on the design of the detector, these ion hits are either recorded directly or imaged via an ultrafast imaging camera. This section details the design of the different detectors and cameras used to record the produced ions.

3.3.1 Detectors

MCP + Phosphor Detector

The detectors used at both FLASH and the University of Oxford comprised two Micro Channel Plates (MCPs) and a phosphor screen. Each MCP primarily consists of an electrically insulating material, lined with a large number of evenly arranged channels with diameters in the low micrometres. The wall of each channel is layered with a semiconductor, chosen to enable high secondary electron emission, and hence electron amplification. Each side of the MCP has a metallic layer applied, enabling a voltage to be applied to electrodes to accelerate electrons. The MCP pores are chevron stacked, ensuring that particles collide with the walls of the channels (Figure 3.7(a)). Therefore, during experimental operation ions enter the channels of the MCP and collide multiple times with the channel walls. This results in additional electrons being released, which can in turn also collide with the channel

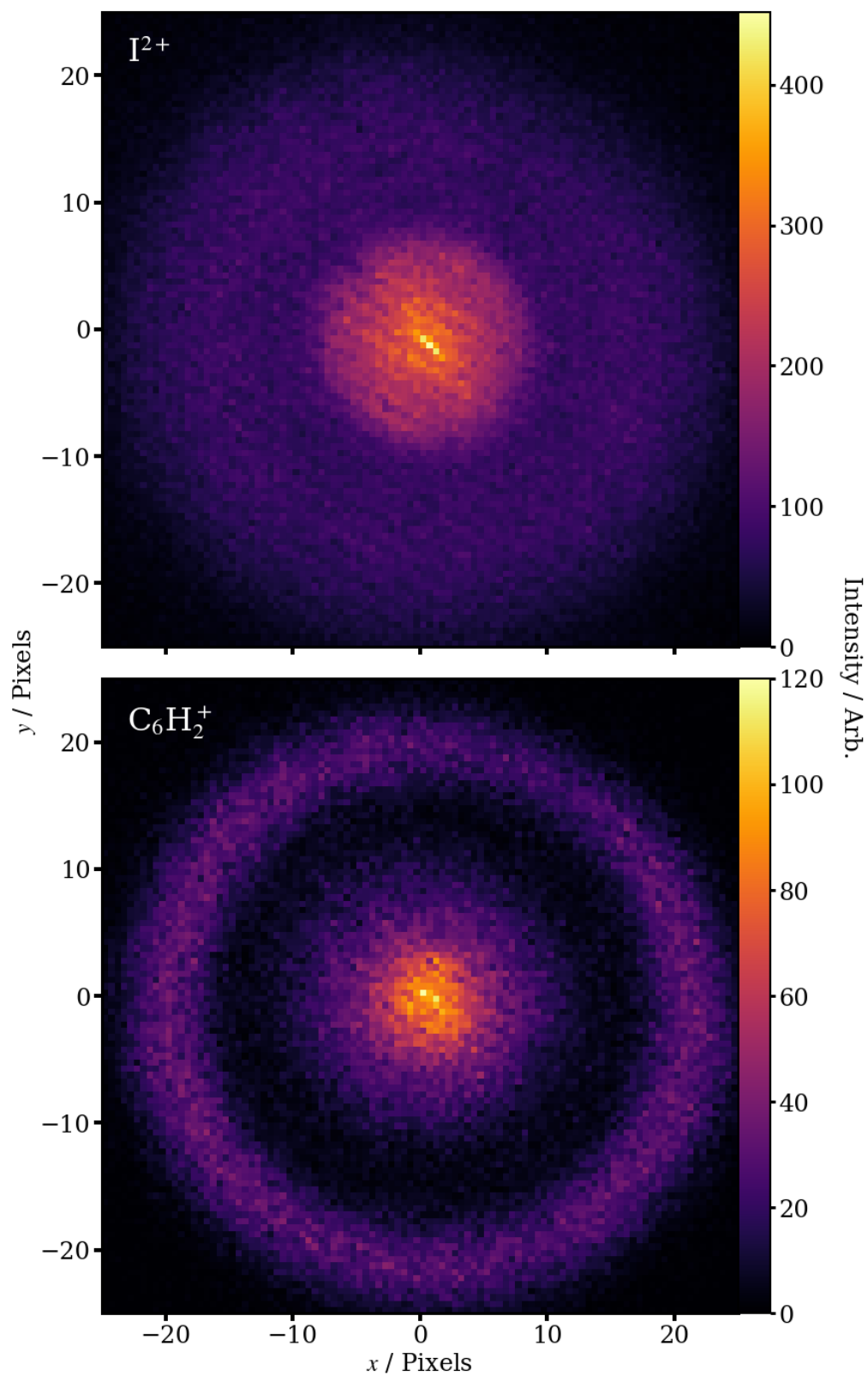


Figure 3.6: Example ion images for I_2^+ and C_6H_2^+ recorded during the Coulomb explosion of iodobenzene.

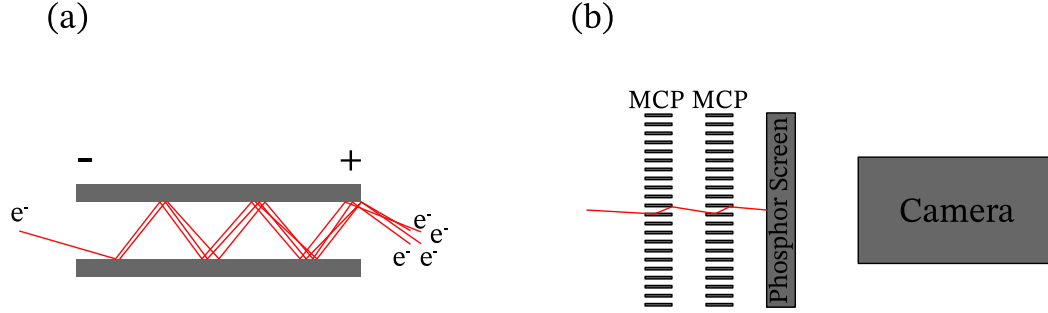


Figure 3.7: (a) Schematic representation of signal amplification in an individual channel on an MCP. A single electron collides with the wall of the channel, prompting secondary electron emission. Provides high signal amplification with minimum loss of spatial information. (b) Schematic showing how multiple MCPs can be coupled with a phosphor screen and a rapid imaging camera to record events. Voltages are applied to the MCPs and the screen to accelerate electrons. For the experimental setup at the University of Oxford, these voltages corresponded to 800 V on the ‘back’ MCP, and 5500 V on the screen, with no voltage applied to the ‘inner’ MCP.

walls and cause further electron release. The voltage applied to the MCP ensures electrons are rapidly accelerated across it, and the output electrons have a similar spatial distribution to the input. This therefore allows easy signal amplification for detection, with minimal loss in spatial resolution. Coupling multiple MCPs in series enables further amplification with electrons passing from the first plate to the second. After passing through the MCPs, the electrons are accelerated towards a high voltage phosphor screen, which is illuminated at the collision location of the particle. This illumination of the detector is then recorded by a rapid imaging camera (such as PImMS2 or TimePix3, which will be described later) (Figure 3.7(b))[61, 62]. The detector at FLASH is an ‘Avalanche PhotoDiode (APD) 2 PS 75/12/10/8 | 60:1 AU P47’ detector, which corresponds to the detector having two chevron stacked MCPs with a quality diameter, pitch, pore size, bias angle, aspect ratio, MCP coating and detector type of 75 mm, 12, 10 μm , 8° , 60:1, gold and P47, respectively. The detector at Oxford is a ‘Vacuum Imaging Detector (VID) 2 PS 40/15 | 40:1 P47’ detector, corresponding to two chevron stacked MCPs, with a quality diameter, pore size, aspect ratio and detector type of 40 mm, 15 μm , 40:1 and P47, respectively.

Delay-Line Detector

Unlike the FLASH and Oxford experimental setups, rather than using a phosphor screen and rapid-imaging camera, the experimental setup at SACLA uses a hexanode delay-line detector. This detector consists of three sets of wires orientated at 120° to each other, forming a hexagonal shape (Figure 3.8).

When a particle interacts with the hexanode detector, it causes an electron signal in each set of wires, which travels in both directions towards either end of the wire. The arrival time at each end of the wire is recorded, and the difference between the two calculated. Combining this with the speed of the signal allows the determination of where in the wire it originated, and hence the position in the detector it originated at. This provides extremely accurate measurements of both the ion's interaction location, as well as the ToF, and allows accurate measurements of the ion's momentum[63]. There are advantages and disadvantages to delay-line detectors and MCP/phosphor screen detectors. MCP/phosphor screens are able to record very high ion count rates, but are less effective at recording accurate ion momenta. Conversely, delay-line detectors record very high accuracy momentum information, but struggle with high count rate experiments.

3.3.2 Cameras

Pixel Imaging Mass Spectrometry Camera

The Pixel Imaging Mass Spectrometry (PIImMS) camera, equipped with a PIImMS2 sensor, was focused on the experimental detector, and records activations from ions interacting with the detector. The PIImMS2 sensor is a Complementary Metal-Oxide Semiconductor (CMOS) sensor, that measures activations on the detector over a specified threshold. Any signals above this threshold are recorded as an ion 'hit'. The sensor is 324×324 pixels, with a time resolution of 25 ns, and can function at a repetition rate of up to 50 Hz. For each ion that interacts with the detector, the sensor records the (x,y) position of the ion, along with its interaction time with the detector, t , relative to an external trigger. The PIImMS camera is capable of imaging multiple fragments during a single laser cycle, which is

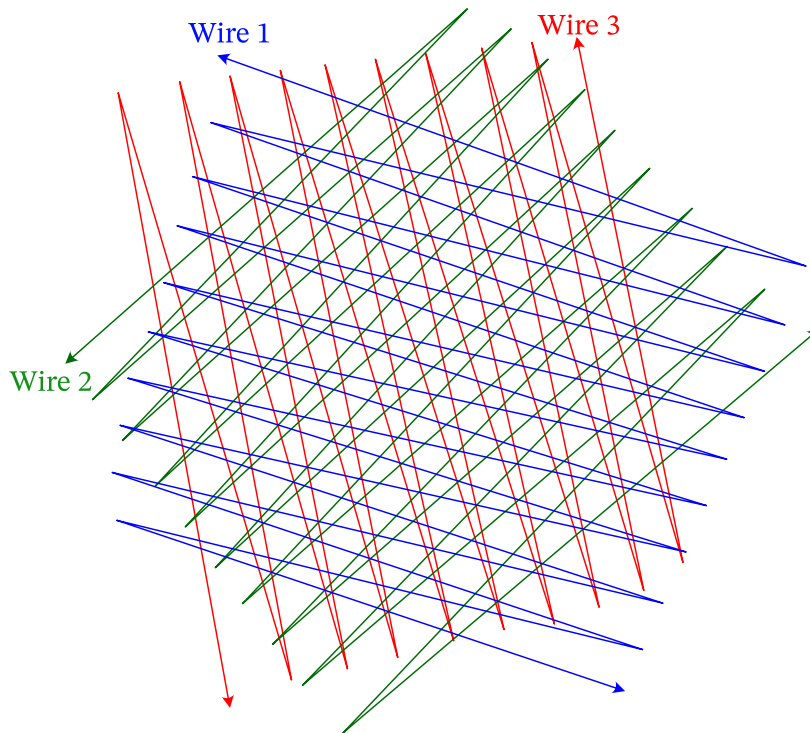


Figure 3.8: Configuration of the three sets of wires used in a hexanode delay-line detector. Each wire is orientated at 120° to the others.

beneficial for the study of larger molecules, due to the higher likelihood of multiple fragmentation pathways occurring[64].

TimePix Camera

The original TimepixCamm, which again uses a CMOS sensor, was developed by Fisher-Levine and Nomerotski and utilised a 256×256 pixel sensor with a time resolution of 20 ns[65]. In addition to PImMS2, the later generation Timepix3 (Tpx3) camera was used for data collection. Tpx3 has several distinct differences to the original chip and PImMS2. While it still utilises the same 256×256 sensor as the original chip, the readout chip has been sufficiently improved to enable a time resolution of 1.6 ns. The pixels have a much improved processing time ($\sim 0.5 \mu\text{s}$ downtime), which allows each pixel to detect multiple hits during a single laser cycle[66]. Tpx3 also records both an ion's Time-over-threshold (ToT), which is a measure of when the signal amplitude is above a certain threshold, and

Time-of-arrival (ToA) which measures the incident time of the signal. A large ToT is found to correspond with a short ToF width for a given peak, and this correlation is used to correct the ToF spectrum. After explosion, depending on the orientation of the molecule, the fragments can possess momenta either towards or away from the detector (the front and back of the Newton sphere described in Section 3.2.1). The ion optics will direct all fragments towards the detector, but this difference in initial momentum leads to slightly different ToFs for ions produced in the same event but in different molecules. The benefit of TimePix's accurate ToF measurement and the short downtime of each individual pixel is these slight variations in ToF can be measured, allowing accurate measurement of ion momentum. This is possible as each pixel is capable of detecting one ion, resetting, and then detecting an additional ion that is produced later in the laser cycle, with the same (x,y) coordinates, but a different time value[67, 68].

3.4 Data Processing and Analysis

After the ions have interacted with the detector and been recorded, several processes are applied to increase ease of analysis. These are centroiding the data and converting from radius to kinetic energy/momentum. After processing, the time-resolved data was primarily analysed through its momentum distribution representation, or via covariance analysis. All of these processes are described below.

3.4.1 Centroiding

Due to the nature of the detectors and cameras used for data acquisition (such as the time resolution of the camera), a single ion can create a flash of multiple photons, which illuminates multiple pixels simultaneously, or appear in multiple time-bins. Multiple pixels of the detector being lit by one ion can lead to an over-reporting of ion hits, as the camera cannot identify whether the pixels were lit by multiple ions or a single ion. Additionally, in some cases independent clusters of ions that hit the detector in similar locations can accidentally be grouped together into a single cluster if adjacent pixels are illuminated. To account for this, data is centroided,

which assigns ion hits to single pixels and time-bins. One such way that this occurs is by finding the Gaussian centres of individual clusters, and specifying maximum cluster sizes centred around that bright central pixel, which helps prevent any overlap of adjacent clusters[69]. Alternatively, weight can be assigned to the earliest hit that occurs, which corresponds to the brightest signal and therefore usually to the centre of the cluster and the most accurate signal. Many different centroiding protocols can be applied, and details of any centroiding method are referenced where relevant. Centroiding for the University of Oxford data was accomplished using the method described by Slater[70], which calculates the coordinates of the centre of each cluster by using a weighted average of each pixel that comprises the cluster. The coordinates of the centre are given by Equation 3.5:

$$C = \frac{\sum_{i=1}^n r_i t_i^{-1}}{\sum_{i=1}^n t_i^{-1}}, \quad (3.5)$$

where t_i is given by Equation 3.6 with T_i and T_0 being the time-bin of the i th pixel and the earliest event in the cluster respectively, and r_i is the i th pixel coordinate.

$$t_i = T_i - T_0 + 1 \quad (3.6)$$

Limits were chosen to specify the maximum cluster size and time windows that are considered. Figure 3.9 shows an example of data pre- and post-centroiding from the experimental setup at the University of Oxford, where cluster size and time-bin values were chosen to obtain approximately Poissonian distributions of ion hits.

3.4.2 Determining Fragment Kinetic Energy

The PImMS or TimePix cameras record the x and y positional data of each ion hit on the detector. This provides a value for the radius from the centre of the detector for each ion interaction. The relationship between distance from the centre of the detector, and kinetic energy of the incident ion is non-linear (shown in Equation 3.4 in Section 3.2.1). As such, to convert the radius information to the more useful kinetic energy (and subsequently momentum) values, the SIMION software package was utilised. Using a scaled digital representation of the experimental setup at the

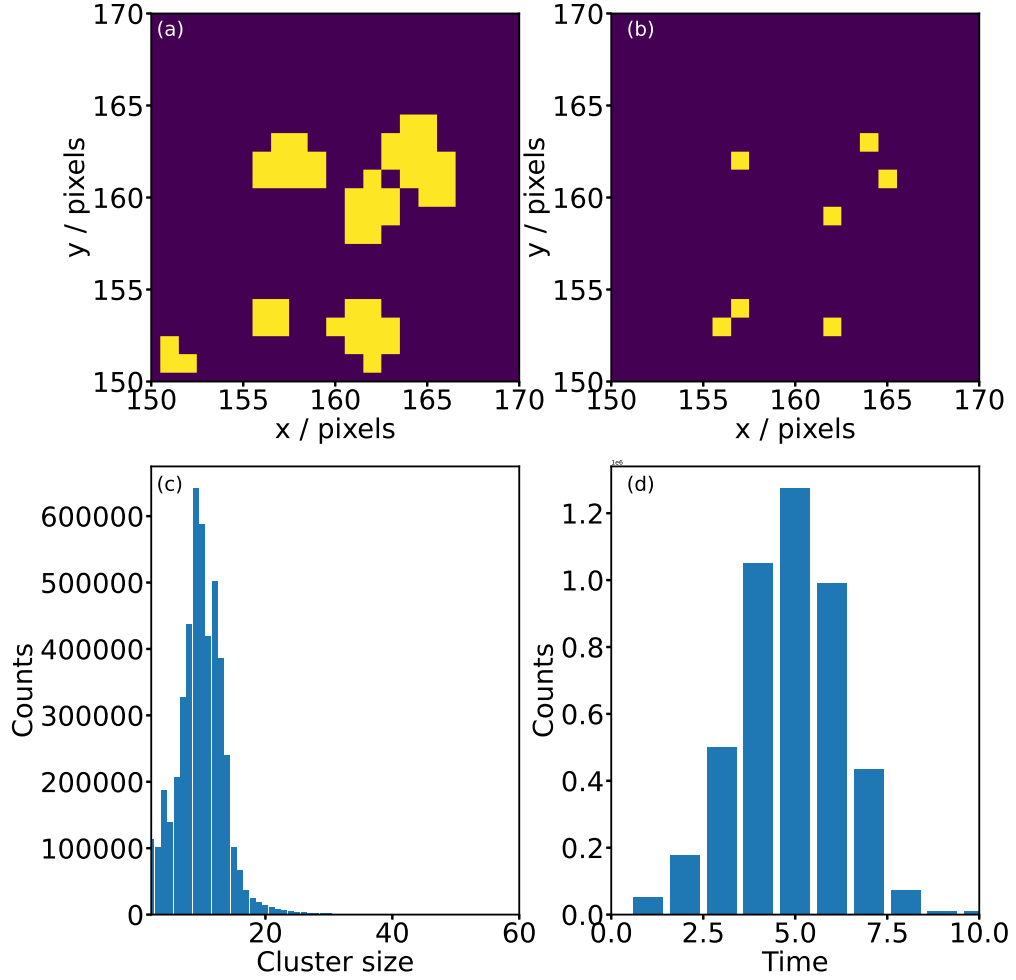


Figure 3.9: Example centroided data from the in-house experimental setup at the University of Oxford. (a) shows the raw uncentroided data obtained from the experiment. (b) shows the data after the algorithm has been applied and the centre of each cluster has been found. (c) and (d) show the distribution of cluster sizes and time-bins for the data.

utilised facility (the accuracy of which has been validated by previous experiments), ions can be directed along the virtual ToF tube with different kinetic energies, and their corresponding positional detector information measured. Fitting this relationship between ion kinetic energy and detector position with a multi-order polynomial provides conversion coefficients that can be applied to the data obtained on physical experimental setups[71].

3.4.3 Momentum Distributions

Throughout the following chapters, the ion data will primarily be displayed using a time-dependent momentum distribution representation. This is produced firstly by

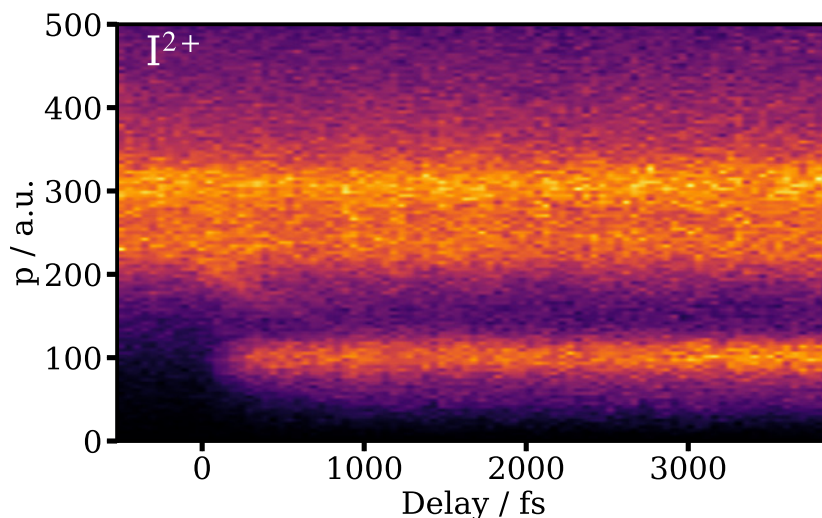


Figure 3.10: Example I^{2+} momentum distribution, showing ion momentum as a function of time. Normalised by shots per delay bin and probe energy per delay bin.

filtering the entire ToF spectrum on manually chosen ToF regions, which correspond to individual ions (or in some rare cases multiple ions that have overlapping m/z). For each filtered ion, the positional data for each hit in this ToF range is converted into kinetic energy and subsequently momentum. The data are then filtered into manually chosen delay bins, depending on the steps used on the delay-stage in the experiment. Narrower bins allow finer changes in dynamics to be resolved, but consequently lead to fewer statistics per bin. A 3D plot of momentum against delay is then produced (an example of which is given in Figure 3.10 for I^{2+} from the Coulomb explosion of iodobenzene), which allows changes in fragment hit count at particular momentum along the delay range of the scan to be followed. The data in each delay bin is normalised by number of laser shots per bin, to account for regions with higher and lower statistics, and also by the average energy of the probe pulse per bin, to account for any fluctuations in the probe energy during a long data acquisition cycle.

3.4.4 Covariance Analysis

For experiments where multiple fragments from many different reaction channels are being detected, different analytical techniques can be applied to determine the reaction channel of origin for each fragment. For instances where less than one

molecule is exploded per laser shot, and therefore there are only a small number of ions produced, coincidence imaging enables the determination of the geometry of the parent molecule. Coincidence imaging functions by initially taking the detected ion coordinates (x, y and t) and using each ions mass-to-charge ratio to obtain their velocity vectors (v_x , v_y , and v_z). A full data-set is created by iterating through the different fragments. The ‘real’ coincidences are extracted from this parent data-set by ensuring momentum is conserved when comparing the fragment momenta to the momentum of the parent system. Using these real coincidences, fragments produced during the same ionisation event can be determined, and hence their geometries at time of explosion can be calculated, by determining the total forces and trajectories acting on each fragment, using Equation 3.7[72, 73].

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \sum_{j \neq i}^n \vec{F}_{ij} = \sum_{j \neq i}^n \frac{k q_i q_j \hat{r}_{ij}}{|\vec{r}_{ij}|^2}, \quad (3.7)$$

where n is number of fragments, $\vec{F}_{ij}$ are the forces arising from pairwise interactions between fragments i and j , m corresponds to fragment mass, k to the Coulomb constant of $8.987 \times 10^9 \text{ Nm}^2\text{C}^{-2}$, q to fragment charge and $\vec{r}_{ij}$ to fragment separation[73].

While coincidence imaging is excellent at identifying fragments for small counts per laser pulse, it struggles to accurately determine coincident fragments with higher counts. Mikosch and Patchkovskii found that the relative systematic error of a coincidence experiment increased linearly with ionisation event rate, and so coincidence imaging is best suited when the number of ionisation events is small. Due to the limited time available at beamtimes, the FELs are run at a high count rate, to enable a high signal to noise ratio for the desired reaction data to be acquired. Running the FELs at this high count rate makes using coincidence imaging impossible (as it would lead to a high relative systematic error), and as such a different approach, covariance analysis, must be used. Mikosch and Patchkovskii found that in the case of covariance analysis, so long as the noise level can be kept low, the ionisation event rate can often be run at the maximum of the experimental setup[74].

Two-Fold Covariance Analysis

Covariance imaging allows fragments produced in the same ionisation event to be determined, even when there are too many ion counts and ionisation events per shot for coincidence analysis to be applicable. For two-fold covariance imaging the correlation between two ions, A and B, is determined. This is done by determining the quantity of a property of an ion at a particular shot and calculating its deviation from its mean value determined across multiple shots. The mean value of an ion, $\langle ion \rangle$, is determined in Equation 3.8, where n is the number of experimental laser shots:

$$\langle ion \rangle = \frac{1}{n_{shots}} \sum_i^{n_{shots}} ion_i \quad (3.8)$$

If A and B vary in the same direction (i.e. a similar quantity of A is produced with a similar quantity of B) the covariance is positive, and it is likely the two ions are produced during the same ionisation event. A covariance of zero means there is no correlation between the ions, and a negative covariance means the ions are inversely correlated. The total covariance between two fragments can be determined in two ways, and both forms of this equation are shown below in Equation 3.9.

$$Cov(A, B) = \langle (A - \langle A \rangle)(B - \langle B \rangle) \rangle = \langle AB \rangle - \langle A \rangle \langle B \rangle \quad (3.9)$$

The first representation, shown in the first half of Equation 3.9, calculates the deviation of A and B from their mean values respectively and subsequently their covariance. The second representation initially calculates all possible correlations, $\langle AB \rangle$, and then estimates the false correlations, $\langle A \rangle \langle B \rangle$, which are from ions produced in different reactions channels, and subtracts them, providing the covariance. This is shown pictorially in Figure 3.11 for a simulated two-body Coulomb explosion. Shown are the images resulting from the total correlations, the false correlations, and the resultant covariance image where a strong 180° recoil feature is seen as expected from a two-body back to back recoil [73, 75–77].

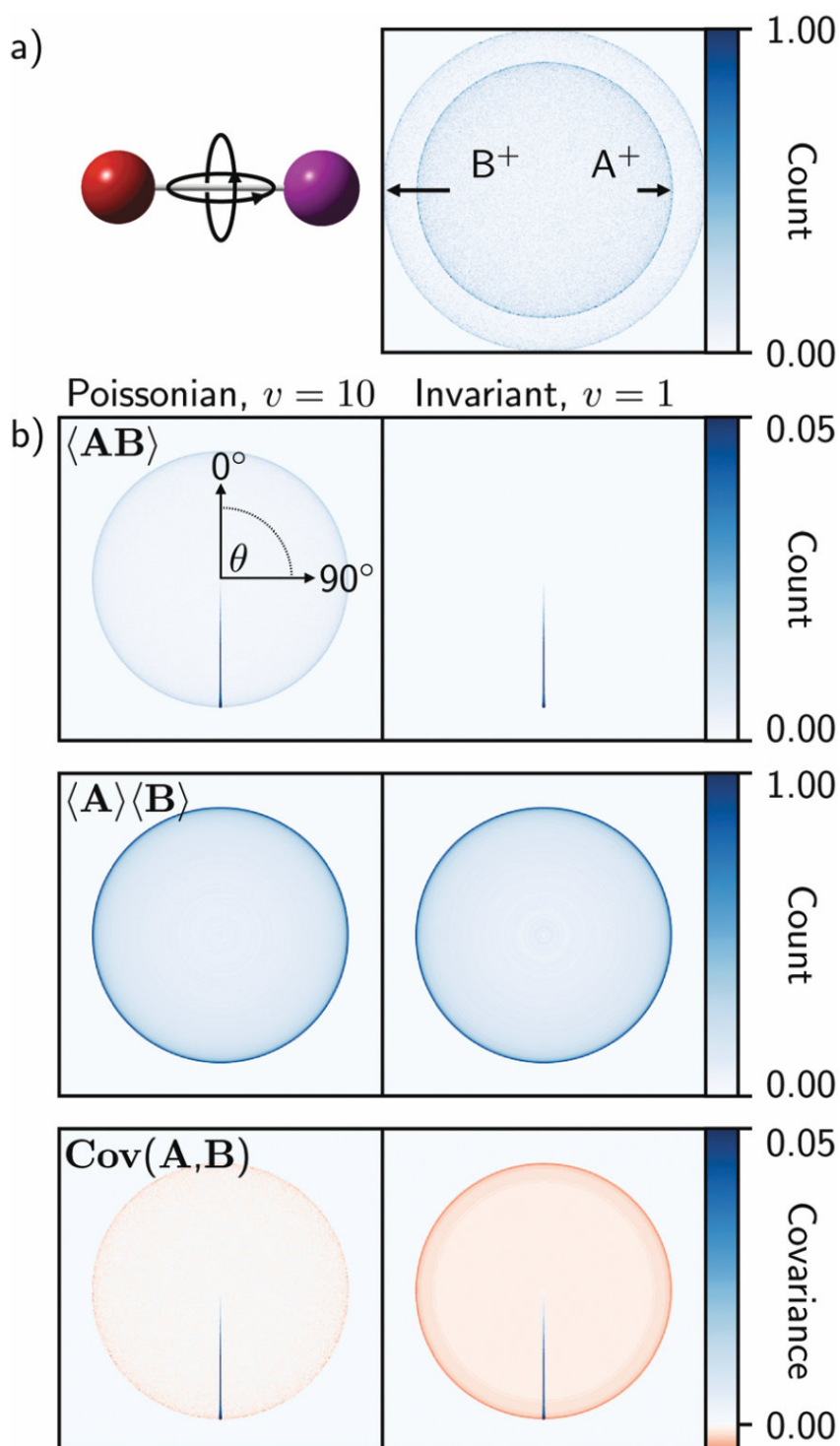


Figure 3.11: (a) Simulated CEI ion images for a two-body explosion. (b) Example of the total and false correlations, and resultant covariance for this reaction. A strong 180° recoil is seen as expected for a two-body explosion, for an event rate, ν , of 10 and 1, respectively. Reproduced from Ref. [73] with permission from the PCCP Owner Societies.

Contingent Covariance

One property of FELs that can limit the effectiveness of covariance analysis is that their pulse energy can fluctuate from shot-to-shot. This fluctuating energy can lead to different fragmentations occurring between different shots, which can lead to false correlations (as a higher energy probe pulse predictably leads to higher count rate, irrespective of if they're being produced in the same reaction channel), and hence an inaccurate determination of the covariance[78]. This variation in FEL energy can be largely accounted for using a process called contingent covariance mapping.

Contingent covariance is implemented by slicing the full data-set into smaller sections of equal statistics, using the fluctuating value as a slicing parameter (for the data presented in this thesis, FEL pulse energy, an example of which is shown in Figure 3.12). By grouping the data into slices that contain narrower ranges of FEL energy, the covariance of each individual slice may be determined, and then subsequently averaged to give a covariance for the full data-set. As each slice only contains shots with similar FEL energies, the false correlations due to the fluctuating pulse are greatly limited. This implementation is illustrated by Equation 3.10:

$$ContingentCovariance(A, B) = \frac{1}{N} \sum_1^N Cov(A, B) \quad (3.10)$$

Where N is the number of slices the parent data-set was divided into. To account for the upper and lower edges of the FEL pulse energy having a lower shot count than the energies around the mean, non-linear bin sizes were utilised in this thesis, with bin sizes determined to produce an equal number of shots per slice. The number of slices chosen should also be small enough that the statistics per slice are sufficient to still estimate the mean value of the chosen ions[76, 79]. Applying this contingent covariance method allows for any non-linearity in the correlation with the chosen fluctuating parameter to be accounted for, and so is suited for situations in which multiphoton ionisation may occur[80].

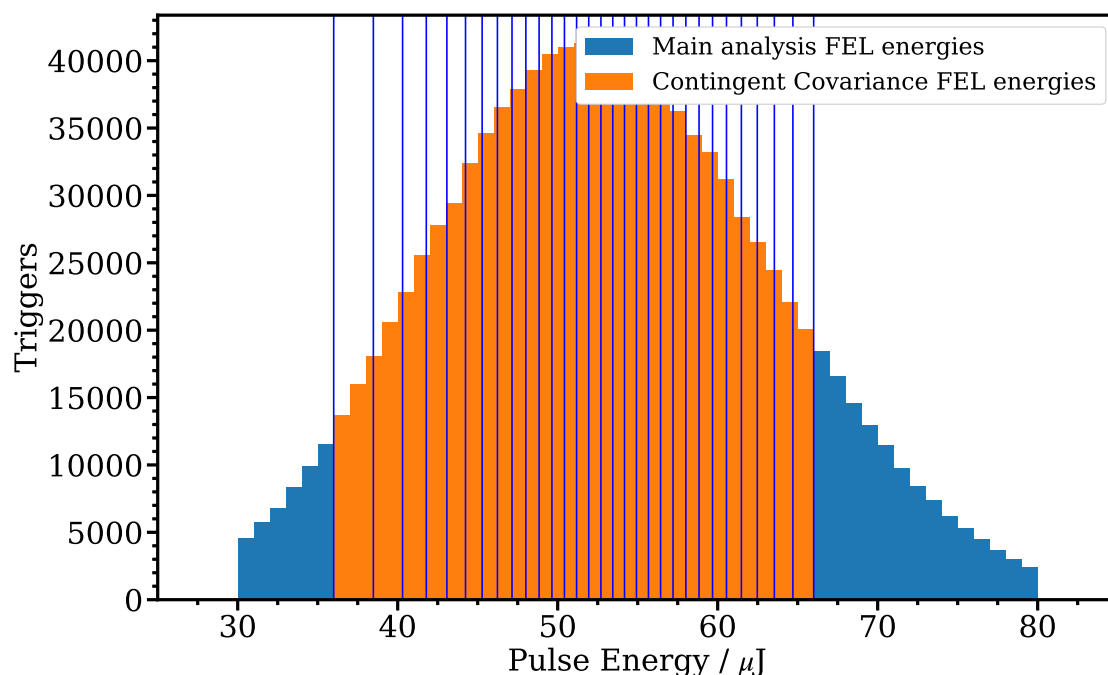


Figure 3.12: Example histogram showing how the total FEL energy distribution is separated into bins for contingent covariance.

3.4.5 Covariance Representations

There are multiple different ways of representing covariance information that allow different molecular parameters to be more easily observed or determined. The representations utilised throughout this thesis are outlined below.

Time-of-Flight

A ToF-ToF covariance map, as shown in Figure 3.13, shows a representation of the correlations between every pair of fragments in the molecular ToF. For each fragment with a unique ToF the covariance is calculated between every other fragment's ToF as described in Equation 3.9. This results in a covariance matrix, S_t , as shown in Equation 3.11 for a system with five ToF values, where s_{ab} corresponds to the covariance between ToFs t_a and t_b .

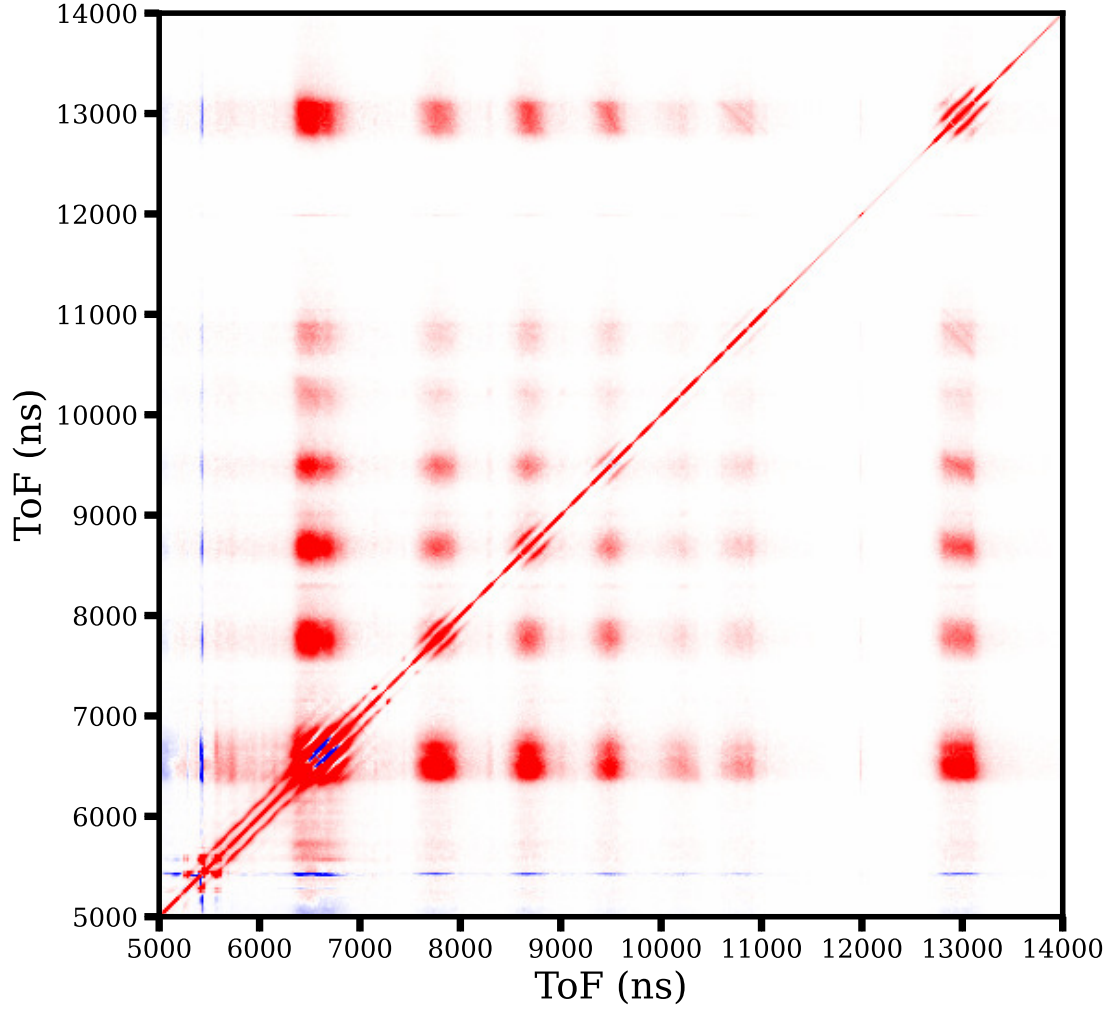


Figure 3.13: Example of a ToF-ToF covariance map. Diagonal lines indicate that the ions located at those time-of-flight peaks are covariant. The autovariance runs diagonally from (5000,5000) to (14000,14000) and represents an ion being self-covariant. Regions of red positive intensity correspond to ion pairs being correlated. While regions of blue intensity corresponding to negative covariance.

$$S_t = \begin{matrix} & \begin{matrix} t_1 & t_2 & t_3 & t_4 & t_5 \end{matrix} \\ \begin{matrix} t_1 \\ t_2 \\ t_3 \\ t_4 \\ t_5 \end{matrix} & \begin{bmatrix} s_{11} & s_{12} & s_{13} & s_{14} & s_{15} \\ s_{21} & s_{22} & s_{23} & s_{24} & s_{25} \\ s_{31} & s_{32} & s_{33} & s_{34} & s_{35} \\ s_{41} & s_{42} & s_{43} & s_{44} & s_{45} \\ s_{51} & s_{52} & s_{53} & s_{54} & s_{55} \end{bmatrix} \end{matrix} \quad (3.11)$$

Pairs that are likely produced in the same event are visible as sharp lines of positive covariance, with non-correlated fragments showing up as regions of zero covariance. A constant line of positive covariance known as ‘autovariance’

is visible running diagonally through a ToF covariance map, and is the result of any individual ion naturally being covariant with itself. This representation provides a convenient method to determine which fragments are produced from the same Coulomb explosion, and helps inform decisions over which ion pairs to perform more detailed analysis on.

Recoil-Frame Covariance

Recoil-frame covariance mapping calculates, and displays, the covariance between spatial positions of ion hits on the detector, for each pixel on the detector for a chosen pair of fragment ions, using equation 3.9[77]. An example of this for showing the recoil of two ions is shown in Figure 3.14. One benefit of recoil-frame covariance over ToF-ToF covariance is multiple features corresponding to multiple dissociation channels are more easily distinguishable. In Figure 3.14 these are visible as a feature at 180° corresponding to a two-body recoil, and an off- 180° feature corresponding to a three-body recoil.

Recoil-frame covariance is determined as follows: initially, for $\text{Cov}(A,B)$, A is defined as the ‘reference’ ion, and the pixels in this image are fixed in place. The other ion, B, is defined as the ‘recoiling’ ion. For each individual pixel in the reference ion image a separate covariance map is generated by determining correlations between each individual pixel in the recoiling ion. This produces N covariance maps, where N is the total pixel count, and an overall covariance image for the two fragments is obtained by summing these N maps (after ensuring each individual map is oriented in the same manner). Details of the determination of the covariance matrix S are given for recoil-frame covariance in Reference [73]. Given that after reorientation the reference ions are all travelling the same direction, the angle between the reference and positive covariance with the recoil ion corresponds to the recoil angle of the two fragments. The radii the regions of positive covariance appear at can be used to determine the velocity distribution of the chosen fragments[77, 79].

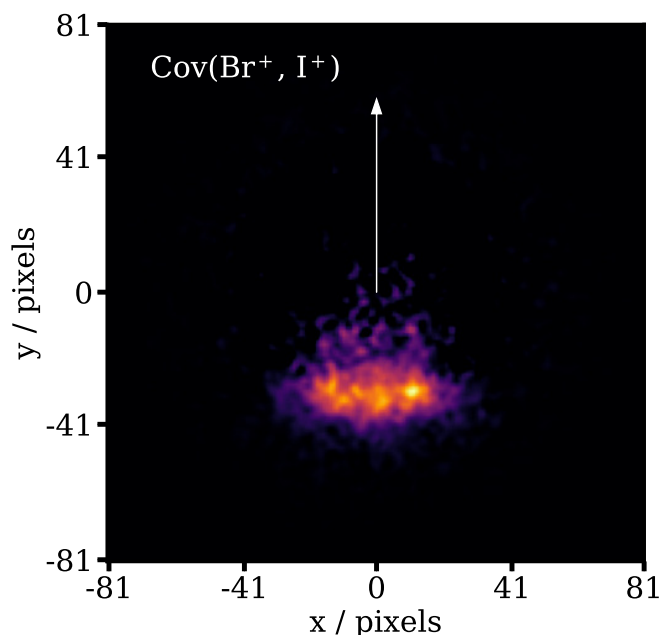


Figure 3.14: Example recoil-frame covariance map between Br^+ and I^+ . The broad positive signal indicates multiple reaction channels are occurring - one where the fragments recoil at 180° , and one where they recoil at $<180^\circ$, indicative of two- and three-body recoils, respectively.

Recoil-Angle Covariance

Recoil-frame covariance mapping represents any correlations between the intensities of two different pixels. An alternative representation is to plot the covariance between the total fragment momenta, p , of two ions as a function of recoil angle β . This representation provides a more accurate determination of the recoil angle between the two ions, and hence any small variations from equilibrium geometry can immediately be distinguished. This representation is therefore most useful when following a reaction where a degree of bending is expected to occur, as shall be seen in Chapter 6. When combined with time-dependent covariance (described below), rapid molecular geometry rearrangements throughout a reaction that lead to a multi-body explosion can be observed as a shifting of the positive covariance along the angle axis. This representation is shown in Figure 3.15 (for a selected set of delay values in a time-dependent data set). The regions of positive intensity correspond to positive covariance, that is, fragments with that specific momenta and bend angle are correlated, and therefore give an indication of the geometry of

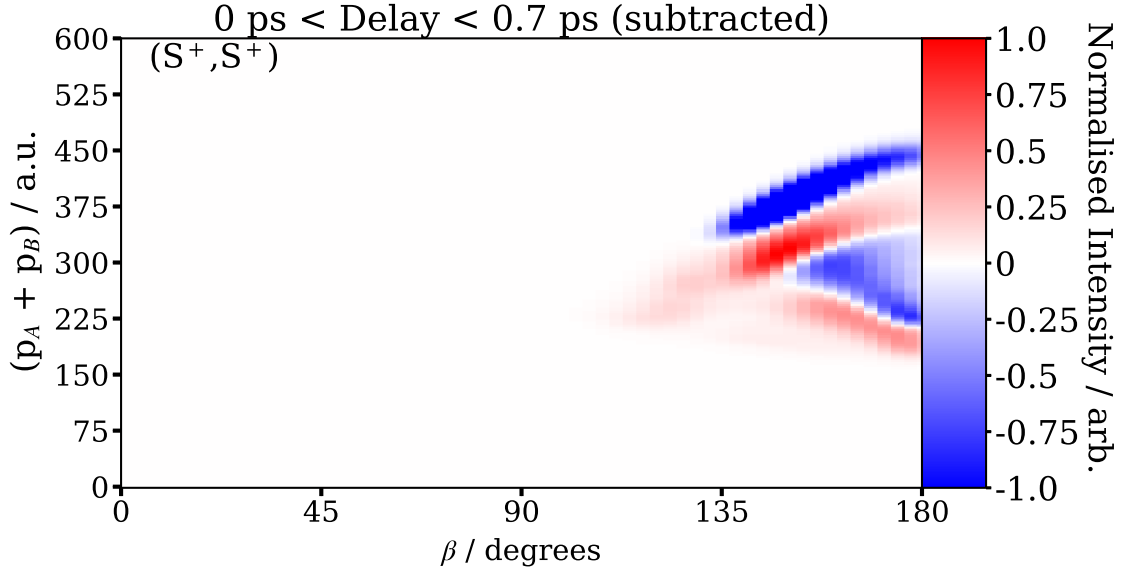


Figure 3.15: Example recoil-angle covariance map between S^+ and S^+ , from the Coulomb explosion of CS_2 , showing summed fragment momenta as a function of recoil angle. Positive intensity corresponds to the two ions being correlated, negative intensity corresponds to two ions being inversely correlated.

those two atoms at the time of explosion. Regions of negative intensity correspond to negative covariance, indicating that the fragments are inversely correlated[45].

Time-Dependent Covariance

For a two-colour experiment all of the above representations can be further refined by calculating changes to covariance as a function of time. If data is filtered by pump-probe delay and covariance calculated for each range, the covariance can be calculated for these delay values independently. This enables the effect of pump-probe delay on molecular properties to be observed (for example the molecular geometry can be compared between probing shortly after excitation, and when a longer period has elapsed, where potentially the fragments may recoil at different angles). An example of this is given in Figure 3.16, for the recoil of two S^+ ions at short and long delays between excitation and Coulomb explosion. At short delays a region of intensity is seen at $\sim 135^\circ$. This positive covariance is absent at later delays, confirming the transient nature of this feature. Similar to contingent covariance, one factor that must be considered when filtering by delay is that the delay ranges chosen are large enough to maintain an accurate determination of

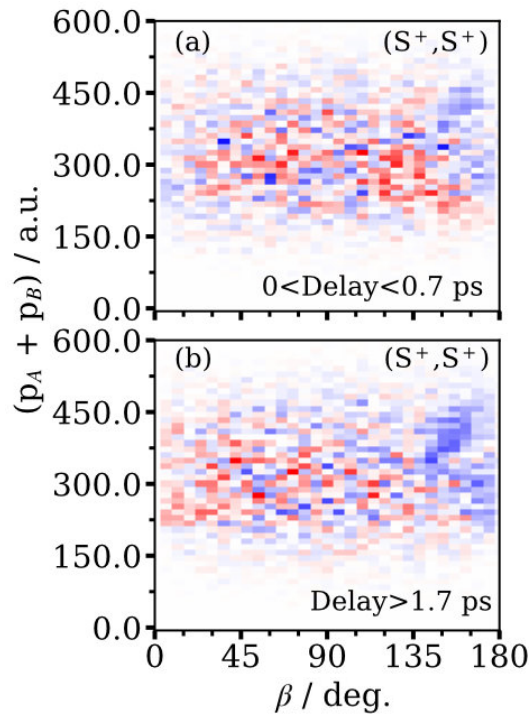


Figure 3.16: Time-dependent covariance image for (S^+, S^+) corresponding to short, (a), and long, (b), delay periods after excitation.

the mean value of each ion, and so for detailed time-dependent studies using fine delay bins a very high statistic acquisition is required.

3.5 Summary

This Chapter has guided the reader through the different stages of a CEI imaging experiment and the subsequent data analysis. Ion generation, direction, detection and analysis were all explored, with the major experimental instruments and methods responsible for each explained.

4

Identifying the Dissociation Products of the Photodissociation of CH₂BrI

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4.1 Background

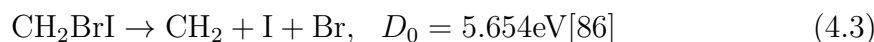
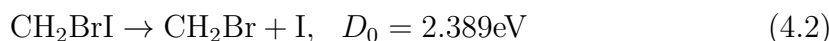
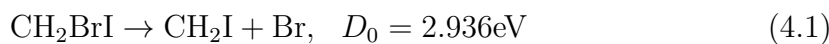
As described in Chapter 1, the data in this thesis demonstrate CEI’s capability to image and characterise ultrafast photodissociation reactions. To that end, this chapter shows how CEI can assign whether a molecule dissociates via a two- or three-body mechanism, using a simple halogenated molecule, bromiodomethane, CH₂BrI. Many halomethanes are involved in catalysing the depletion of ozone, and understanding the dynamics of simple halomethanes has the potential to give understanding of the more complicated dynamics of larger halogenated structures[2, 81, 82]. Studying CH₂BrI builds on previous work looking at singly-halogenated

methanes, in particular CH_3I , where the presence of only a single halogen means the molecular centre of mass lies along the C-X bond, which allows C-X dissociation dynamics to be approximated to a ballistic problem, and simplifies any resulting analysis due to the lack of rotational excitation[18, 31, 83, 84]. Here, the addition of a second halogen substituent shifts the centre of mass off the C-X bond, complicating any resultant fragment repulsions, due to rotational excitation of the resultant halomethyl fragment. In addition, the presence of two halogen substituents greatly increases the number of photo-absorption sites, and also increases the density of states, leading to greater wavepacket population crossing of potential energy surfaces. This leads to a variety of excitation routes that can result in one or both of the C-X bonds being cleaved, potentially leading to two- or three-body dissociation mechanisms.

Bond cleavage in CH_2BrI has been found to vary heavily with the excitation wavelength. At 270 nm, an $n(\text{I}) \rightarrow \sigma^*(\text{C-I})$ transition dominates and leads to C-I cleavage. In contrast, at 215 nm, $n(\text{Br}) \rightarrow \sigma^*(\text{C-Br})$ transitions dominate and lead to C-Br cleavage. Despite previous studies finding that C-Br cleavage should significantly dominate in CH_2BrI at wavelengths < 215 nm, the branching ratio has been found to favour C-I cleavage in other molecules such as 1,2- $\text{C}_2\text{F}_4\text{BrI}$, which undergoes C-I and C-Br cleavage in a ratio of 1.7:1 when excited at 193 nm, despite the primary excitation being $n(\text{Br}) \rightarrow \sigma^*(\text{C-Br})$. This was ascribed to rapid energy transfer between the bonds after excitation[85, 86]. As a result, both C-I and C-Br cleavage was expected to occur in this study.

The 202.5 nm UV pulse used in this chapter lies on the edge of the CH_2BrI B-band, which peaks at 218 nm, and so the $n(\text{Br}) \rightarrow \sigma^*(\text{C-Br})$ transition is expected to dominate, leading to predominantly C-Br bond cleavage. Butler *et al.* found that at 210 nm a combination of two-body fragmentation from C-Br cleavage, and three-body fragmentation from both C-X bonds breaking (with some elimination of IBr) occurred with a frequency of 61% and 33% respectively[86]. A similar process was expected to occur here, and an absorption spectrum showing the absorption bands in CH_2BrI is shown in Figure 4.1.

Equations 4.1, 4.2, 4.3 show the most prominent possible fragmentation pathways of CH_2BrI accessible at this UV wavelength, where D_0 corresponds to the bond dissociation energies.



A 202.5 nm photon provides 6.12 eV of energy. Therefore, energetically both bonds can be dissociated via a single UV photon, and a three-body dissociation could occur.

The 13.1 nm XUV probe pulse enables ionisation of both halogen atoms, although the higher absorption cross section of iodine at this wavelength (10 Mb) compared to bromine (1.5 Mb), results in a greater iodine signal. XUV ionisation of the iodine followed by Auger-Meitner decays leads to a highly positive parent molecule. This high charge can redistribute from the iodine to the rest of the molecule, resulting in multiple positive charges repelling against each other, leading to a Coulomb explosion.

The following analysis will first look at the dynamics of the time-independent signal, corresponding to probing of the ground state molecule. This will be followed by the identification of a three-body dissociation mechanism using the time-dependent data. Despite the previous studies suggesting that two-body dissociation is the dominant channel at longer wavelengths, the time-dependent signals observed here imply that at 202.5 nm three-body dissociation dominates. Figure 4.1 gives an overview of the main possible three-body reaction pathways that can occur, with (I) corresponding to probing of the ground state, (II) corresponding to a three-body dissociation with both halogens being charged, and (III) corresponding to a three-body dissociation with one charged and one neutral halogen, where at short fragment separations a charge transfer process (Section 2.5) can occur.

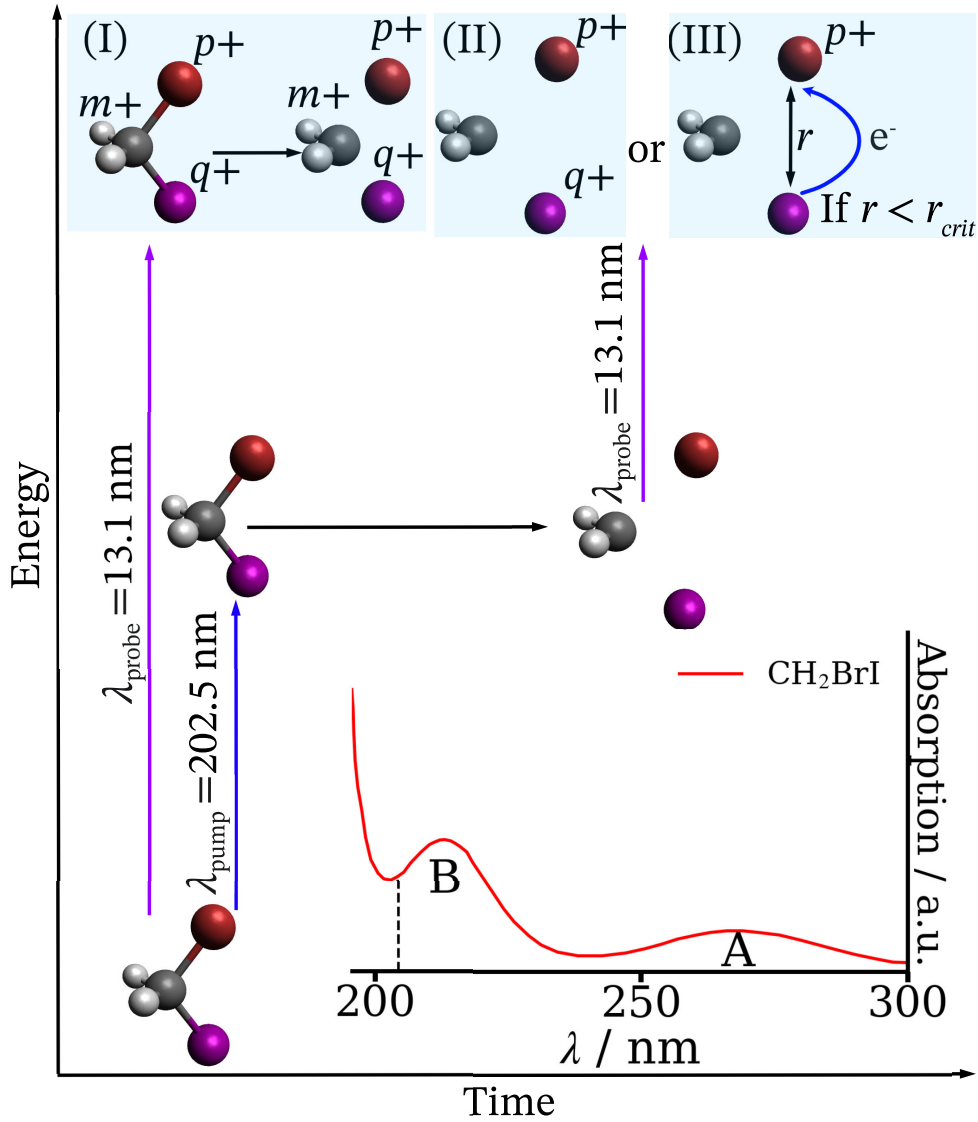


Figure 4.1: Schematic representation of the different three-body reaction channels that can occur for CH_2BrI . The three possible outcomes are: (I) ionisation of the ground state, (II) ionisation of the three-body dissociated state or (III) charge transfer between a charged and neutral fragment following dissociation (described in Section 2.5). Carbon is shown in grey, hydrogen in white, iodine in purple, and bromine in brown. Also shown is the UV-absorption spectrum for CH_2BrI between 198-300 nm, where it can be seen that the utilised pump wavelength (dashed black line) in this experiment excites the molecule on the edge of the B-band[86]

4.2 Methods

4.2.1 Experimental Setup

Measurements were made using 202.5 nm pump and 13.1 nm probe pulses at the CAMP end-station at FLASH[48]. The 202.5 nm pump was produced using the fourth harmonic of an 810 nm, 12 mJ, 57 fs IR pulse. A fraction of this pulse was split into two equal components using a beamsplitter. Two $\beta\text{-BaB}_2\text{O}_4$ (BBO) crystals and several dichroic mirrors were used to frequency triple (via second harmonic generation followed by sum-frequency generation) and subsequently isolate the third harmonic of the IR from the fundamental pulse. The transmitted component of the IR pulse passed through an additional beamsplitter, and the two components produced were reserved for two separate purposes. Firstly, one half of the split pulse was used to produce the fourth harmonic by recombination with the third harmonic via sum-frequency generation. The second was kept for later use in cross-correlation measurements for pulse duration determination. The UV pump pulse was isolated from the recombined pulse using additional dichroic mirrors. The UV energy at the source was measured as 2.5 μJ , which after losses along the beam path gave a UV power at the interaction region of 1.1 μJ . Through determining the cross-correlation of the UV and reserved IR pulse in xenon (and knowing the pulse duration of the IR laser to be 57 fs), a UV pulse duration of 157 ± 18 fs was measured. The UV focal spot size in the interaction region was measured as 38 μm , which gives a calculated UV intensity of $1.3 \pm 0.15 \times 10^{12} \text{ W cm}^{-2}$.

The 13.1 nm XUV probe pulse was tuned to ionise the iodine 4d orbital in CH_2BrI . From the known absorption cross-sections, at this probe wavelength ionisation of the iodine was much more likely compared to the bromine (10 Mb vs 1.5 Mb)[87, 88]. A source energy of $33 \pm 6 \mu\text{J}$ was measured, which after passing through a 101 nm aluminium filter, and accounting for losses along the beam path, gave an interaction region energy of $2.1 \pm 0.4 \mu\text{J}$. Taking previously estimated measurements of the pulse duration and focal spot size by Duesterer *et al.* and Erk *et al.*[48, 89] of 50-60 fs and 10 μm , the XUV interaction region intensity was determined to

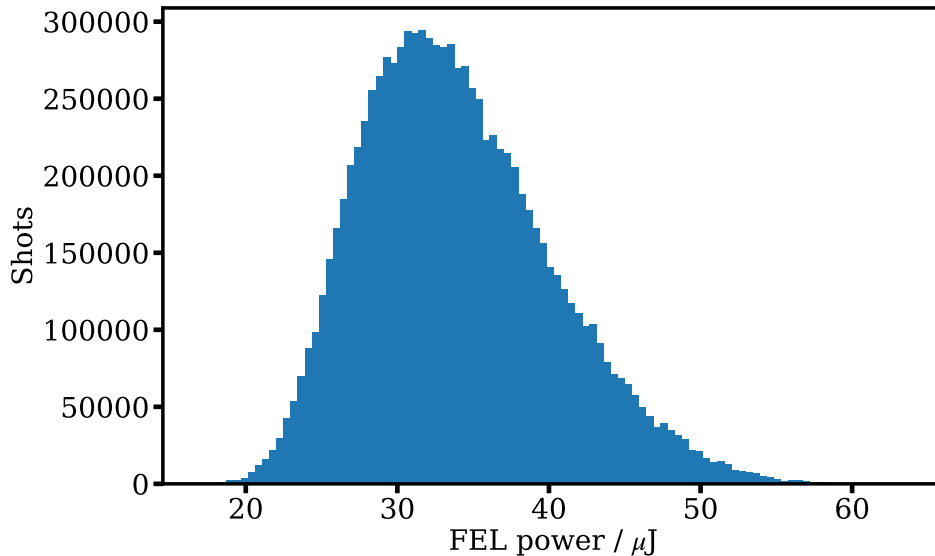


Figure 4.2: Histogram of FEL pulse energies recorded throughout the experiment.

be $9.7 \pm 1.1 \times 10^{13} \text{ W cm}^{-2}$. Figure 4.2 shows the distribution of FEL energies recorded throughout the experiment, measured at the beam source.

These two pulses ran parallel to the detector, and the relative delay in arrival time of the two pulses was controlled by a delay stage in the IR line used to produce the pump pulse. The bunch arrival monitor measured any jitter in the arrival times of the electron bunches of the probe pulse, allowing these variations to be corrected throughout the experiment[90, 91]. The delay stage was operated with a step size of 50 fs. The point at which the two pulses arrived at the same time, t_0 , was determined by a cumulative distribution function (CDF) fit to the yield of Xe^{2+} from ionisation of Xe. This fit is shown in Figure 4.3.

A molecular beam of gas-phase CH_2BrI was introduced to the interaction region perpendicular to the two laser pulses via two skimmers as a continuous jet. A detector comprised of two MCPs and a P47 phosphor screen was used to detect any velocity-mapped product ions, and hits on this detector were recorded using a PImMS2 camera as described in Chapter 3. After collection, the data was centroided to remove interactions where a single photon activated multiple pixels on the detector, according to the process described by Slater *et al*[70, 92].

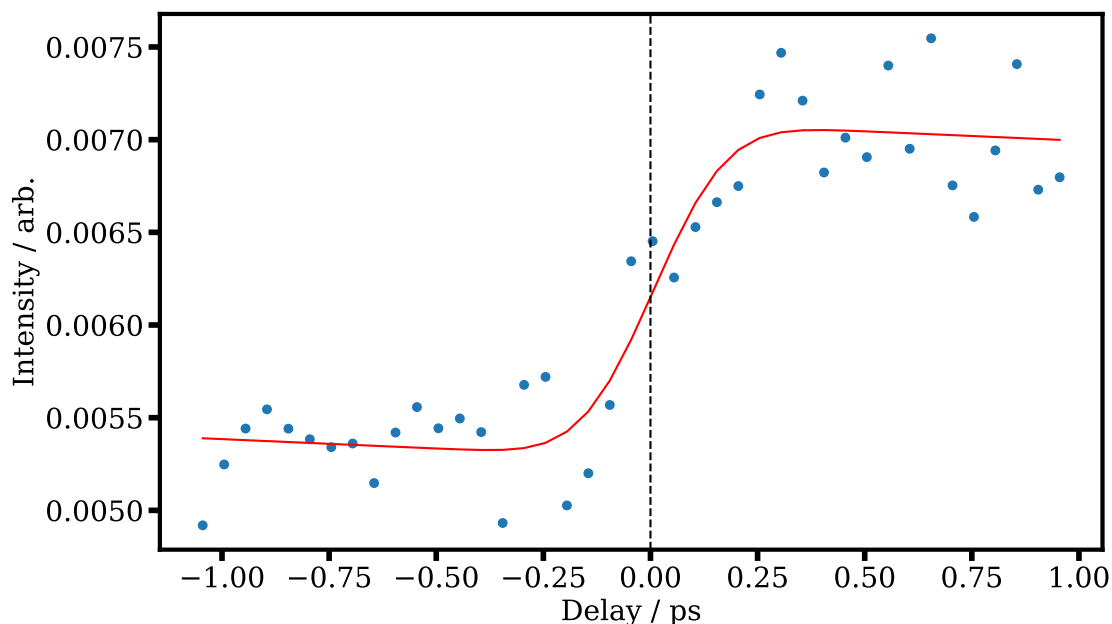


Figure 4.3: Cumulative distribution function fit of the production of Xe^{2+} for the determination of time-zero (the point at which both pulses arrive at the same time) of the pump and probe pulses.

4.3 Results and Discussion

Multiple fragment species originating from the Coulomb explosion of CH_2BrI were detected. Figure 4.4 shows mass spectra produced by the XUV only, and by the UV pulse followed by the XUV. For the two-colour data, the mass spectrum was produced by integrating over all delays after t_0 .

Looking first at the XUV-only data, the following fragments were observed: I^{1-5+} , Br^{1-2+} , CH_2Br^+ , CH_2I^+ and BrI^+ . The lower iodine charge states are attributed to single photon ionisation by the XUV pulse, while multiphoton absorption is responsible for the higher charge states. Xe is isoelectronic to iodine, and obtaining Xe^{4+} requires two photons, meaning the switch from requiring a single to a multiphoton process occurs for iodine charge states $> 3+$ [93]. The fragments are the result of Coulomb explosion of a highly charged parent molecule, produced predominantly by ionisation of the I 4d orbital (and to a lesser extent, due to the lower absorption cross section, by ionisation of the bromine).

Comparing the UV/XUV mass spectra to the XUV-only, the same fragments

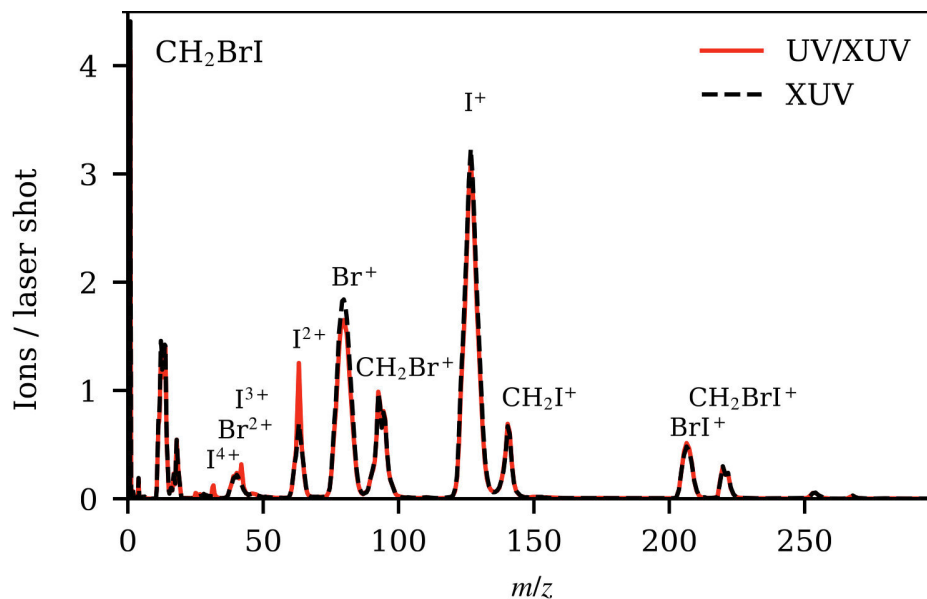


Figure 4.4: Mass spectra for CH_2BrI . Shown in black are fragments detected when the molecule is ionised by the XUV pulse only. Shown in red are fragments detected when the UV pulse precedes the XUV pulse. Data is normalised by number of laser shots.

were detected, however an increase in intensity can be seen in the multiply charged bromine and iodine ions. These enhancements are assigned to ionisation of the halogen after the C-X bond has undergone a photodissociation due to interaction with the UV pulse.

The next section will look at the XUV-only signals, and determine how particular fragments are produced via Coulomb explosion of the ground state parent. Subsequently, enhancements seen in the UV/XUV data will be used to determine the nature of the photodissociation mechanism observed.

4.3.1 Time-Independent Data

The velocity-mapped ion images (Figure 4.5) for each ion were angularly integrated to produce time-dependent momentum distributions for Br^{1-2+} , I^{1-4+} , CH_2Br^+ and CH_2I^+ (Figure 4.6). In this section signals produced via XUV-only interactions will be explored.

Here, and in the time-dependent analysis, the radii of the ion images was converted to kinetic energy using a multi-order polynomial determined via simula-

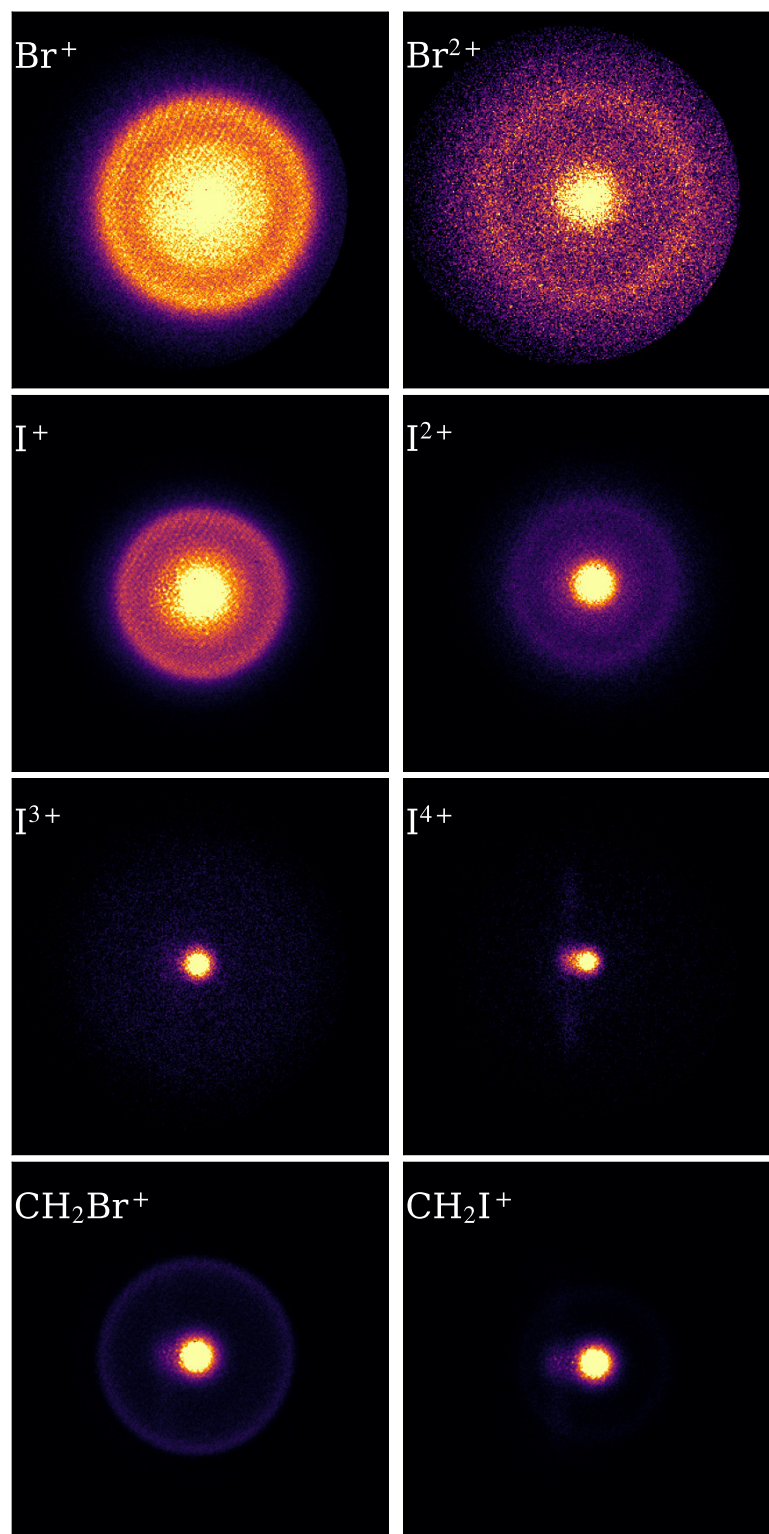


Figure 4.5: Ion images for the ions of interest in the Coulomb explosion of CH_2BrI . These include Br^+ , Br^{2+} , I^+ , I^{2+} , I^{3+} , I^{4+} , CH_2Br^+ and CH_2I^+ .

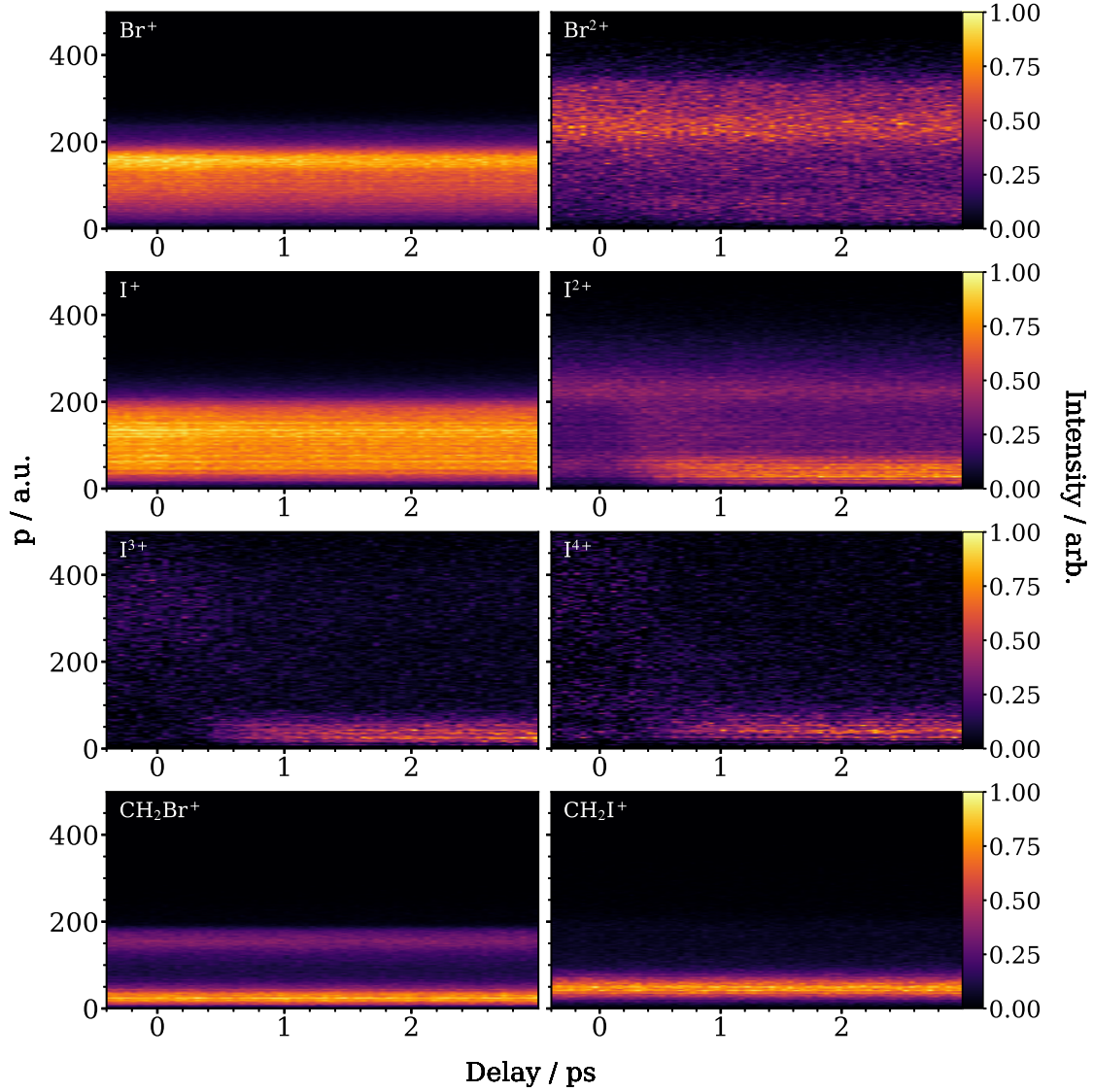


Figure 4.6: CH_2BrI momentum distributions without removing the XUV-only contribution. Ions of interest are Br^{1-2+} , I^{1-4+} , CH_2Br^+ and CH_2I^+ . Intensities in each panel are normalised by number of laser shots per delay bin, and by FEL pulse energy.

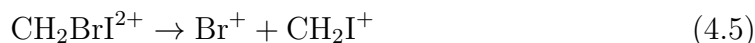
tions with SIMION 8.1 (Section 3.4.2). The central slice of each ion distribution was used, due to the inability of PImMS2 to accurately record 3D momentum information due to its limited ToF resolution.

Several of the ions in Figure 4.6 show only time-independent signal, namely Br^+ , I^+ , CH_2Br^+ and CH_2I^+ . Due to the small structure of CH_2BrI , the only possible fragmentation channel for the production of CH_2Br^+ and CH_2I^+ is a two-body fragmentation into a halogen and halomethyl fragment, dependent on which C-X bond is cleaved. The two channels seen in each of the momentum distributions for

the charged halomethyl cofragment correspond to the halogen fragment being either neutral (low-momentum channel), or in some positive charge state (high-momentum channel), leading to Coulomb explosion. For Br^+ and I^+ there is an additional possible fragmentation pathway: three-body fragmentation into a methyl fragment and two free halogens. These fragmentation channels can again have different momenta dependent on the number and magnitude of charges on the different fragments, and their location on the cofragments.

Recoil-frame covariance analysis, as described in Section 3.4.5, can be used to determine which ions are produced in the same reaction channel, and hence which are the main detectable contributors to the time-independent signals seen in Figure 4.6. Figure 4.7 shows all ion pairs that showed positive covariance from the Coulomb explosion of CH_2BrI .

Starting with the two-body fragmentation channels, positive covariance was seen between $(\text{CH}_2\text{Br}^+, \text{I}^+)$, $(\text{CH}_2\text{Br}^+, \text{I}^{2+})$ and $(\text{CH}_2\text{I}^+, \text{Br}^+)$. For these two-body fragmentation channels only a strong enhancement at 180° is observed, consistent with what would be expected from two charged fragments recoiling against each other. No covariance was observed between $(\text{Br}^{2+}, \text{CH}_2\text{I}^+)$. Therefore, from these covariances, the observed two-body fragmentation channels are shown in Equations 4.4 and 4.5:



Having identified the possible two-body fragmentation channels, the location of the positive charge (i.e. does it reside on the carbon or halogen in the halomethyl fragment) was determined. This was accomplished by first converting the momentum distributions of the relevant channels to velocity, fitting these distributions with Gaussian functions and converting to kinetic energy (KE). An example of these Gaussian fits is shown in Figure 4.8 for the Br^+ distribution, with the feature centred at 2419.3 ms^{-1} corresponding to the two-body explosion, and the lower velocity feature corresponding to the three-body explosion. The low statistics of this

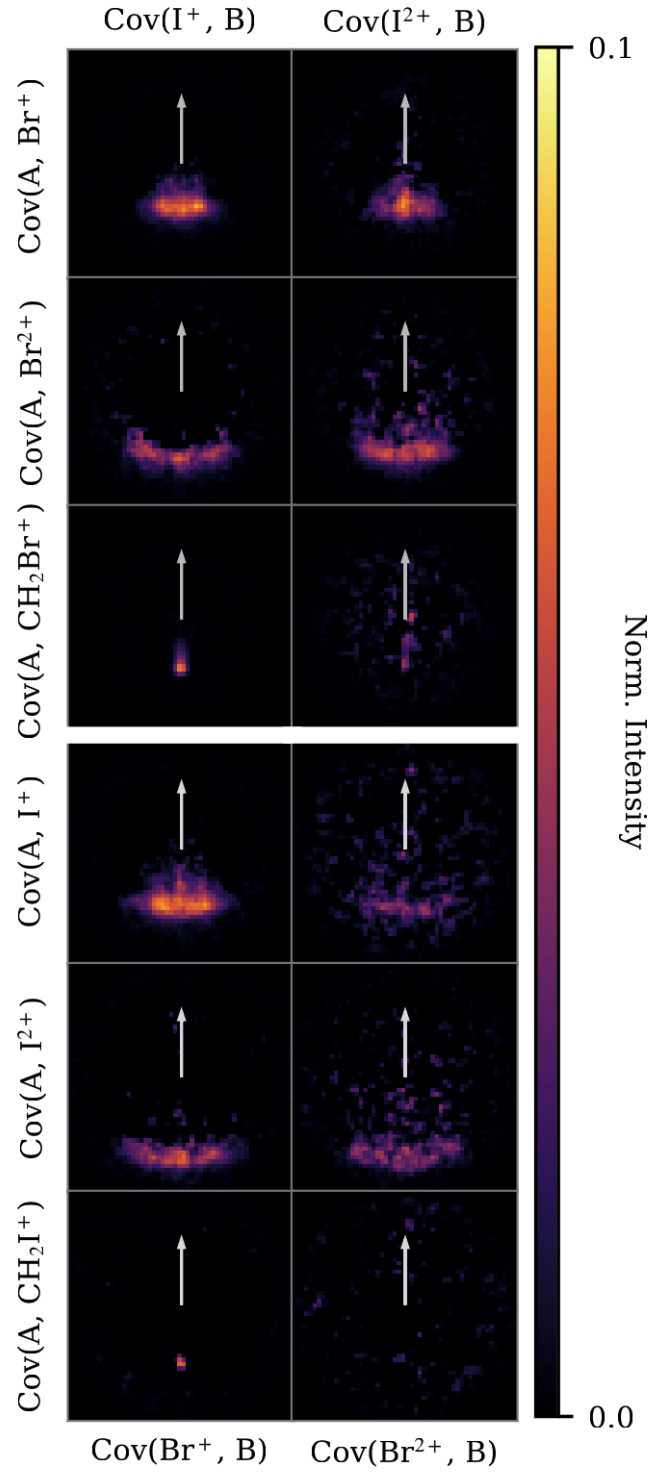


Figure 4.7: All positive recoil-frame covariance signals observed for the time-independent Coulomb explosion of CH_2BrI . Covariance is seen between the following pairs of ions: $(\text{I}^+, \text{Br}^+)$, $(\text{I}^+, \text{Br}^{2+})$, $(\text{I}^{2+}, \text{Br}^+)$, $(\text{I}^{2+}, \text{Br}^{2+})$, $(\text{CH}_2\text{Br}^+, \text{I}^+)$, $(\text{CH}_2\text{Br}^+, \text{I}^{2+})$ and $(\text{CH}_2\text{I}^+, \text{Br}^+)$. Note that it is possible some covariance exists between highly charged iodines and Br^{1-2+} , but the much lower statistics for these ions prevents it from being isolated from noise.

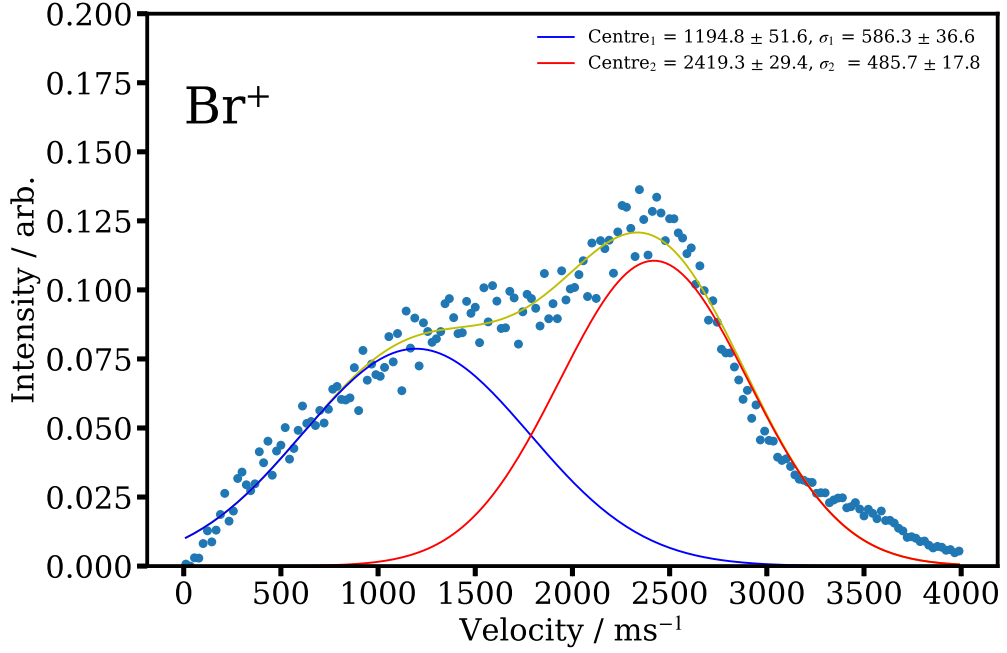


Figure 4.8: Example integrated time-independent velocity distribution for the Br^+ ion from the Coulomb explosion of CH_2BrI . Produced by integrating the momentum distribution data pre- t_0 , to only include signal from the XUV-only interactions. Here and elsewhere in this manuscript the uncertainty of the Gaussian peak corresponds to the uncertainty of the Gaussian fit, while σ corresponds to the standard deviation of the fit.

time-independent analysis are a consequence of the overall goal of the experiment being a time-dependent study, and as such the data presented here is a small slice of the full time-dependent dataset, with delay values chosen to isolate the UV-late data, thus providing a smaller number of shots compared to typical XUV-only experiments. Summing the centres of these Gaussian fits for each charged two-body reaction channel gives the total kinetic energy for each explosion. Subsequently, this kinetic energy can be compared to the predicted kinetic energy for each explosion (Equation 4.6), which accounts for the separation between the two charges, and hence whether the charge is on the carbon or halogen atom in CH_2X^+ . Here and elsewhere in this Chapter, the reported error corresponds to the uncertainty in the Gaussian fit, while σ corresponds to the standard deviation of the fit.

$$\text{KE} = \frac{q_1 q_2 \times 1.6 \times 10^{-19}}{4\pi\epsilon_0 \times R} \quad (4.6)$$

In the above equation q_1 and q_2 correspond to the charges on the two fragments,

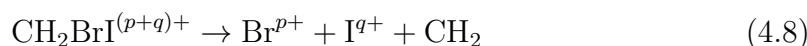
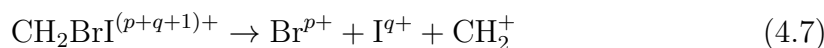
Table 4.1: Experimental kinetic energy as a percentage of predicted energy for two-body fragmentation channels confirmed by covariance. Values are shown for when the positive charge of the halomethyl fragment is located on both the carbon and halogen atom. σ is the standard deviation of the Gaussian experimental kinetic energy fits.

Explosion	CH ₂ X ⁺		C ⁺ H ₂ X	
	KE (%)	σ (%)	KE (%)	σ (%)
CH ₂ Br ⁺ + I ⁺	94	12.3	59	8
CH ₂ Br ⁺ + I ²⁺	87	11	54	7.1
CH ₂ I ⁺ + Br ⁺	97	20	55	11

ϵ_0 is the permittivity of a vacuum, and R is the separation of the two fragments (in this case the C-X (2.089 Å and 1.948 Å for C-I and C-Br respectively) and Br-I (3.247 Å) bond distances). Table 4.1 shows the experimentally observed kinetic energy as a percentage of the predicted kinetic energy by Equation 4.6. From this comparison, the charge is assigned to primarily residing on the halogen atom in CH₂X⁺, with a much stronger agreement between experimental and predicted energies observed. When locating the charge on the carbon atom, the shorter distance between the carbon and halogen atoms produced a much higher predicted energy (due to greater Coulombic repulsion) compared to using the Br-I separation, and so consequently is the less likely location for the charge. It is worth noting that while in the majority of Coulomb explosions the charge resides on the halogen rather than the carbon of the halomethyl fragment, some small number of explosions do occur with the charge residing on the carbon. This is visible as a small peak at $\sim 3600 \text{ ms}^{-1}$ in Figure 4.8, which when converted to kinetic energy and compared to that predicted by Equation 4.6 gives an $\sim 96\%$ agreement between the values.

Moving to the covariance resulting from a three-body fragmentation, a recoil-covariance signal across a wide range of angles is seen with ion pairs of (I⁺, Br⁺), (I⁺, Br²⁺), (I²⁺, Br⁺) and (I²⁺, Br²⁺), and appears as constant higher momenta channels in Figure 4.6. This broad distribution is determined by the charge on the methyl fragment. In the case where two charged halogens and a neutral methyl are produced, the halogens will recoil $\sim 180^\circ$ to each other. However, in the case where the methyl is also charged, there will be an additional recoil component on the halogens, resulting in the broader distribution seen off- 180° . The difference between

these two channels is most noticeable in the covariance between ($\text{I}^{2+}, \text{Br}^+$), where the signal at 180° is more intense than the broad signal, suggesting that in this case, the channel producing a neutral methyl is more likely than that producing a charged methyl. This is likely due to the need for multiphoton ionisation to produce three highly charged species from a parent charge state of $> 3+$. Considering the broad and 180° recoil signals in the three-body explosion, the possible reaction channels are given by Equations 4.7 and 4.8 below. Unfortunately, as the mass of the CH_2 fragment is significantly lighter than both of the halogens, it was not possible to determine covariance between CH_2^+ and X^{n+} , due to the high momentum imparted to the CH_2^+ fragment resulting in it not hitting the detector.



4.3.2 Time-Dependent Data

Of the ions shown in Figure 4.6, four show noticeable time-dependence. These are Br^{2+} , I^{2+} , I^{3+} and I^{4+} . To enhance the visibility of the time-dependent features, an average of the data pre- t_0 was subtracted from each momentum distribution, to remove any XUV-only contributions. The resultant momentum distributions for these four ions are shown in Figure 4.9.

Two clear time-dependent features are visible in each of these ions. Firstly, a depletion at high momentum that occurs at t_0 , which corresponds to a decrease in the ground-state population as a result of an amount of molecules being excited by the UV pulse. Secondly, a constant momentum channel that occurs several hundred femtoseconds after t_0 , and persists to the end of the delay range. It is this channel that shall be the focus of the following discussion. It is worth noting here the lack of any sharply discernable ‘Coulomb distributions’, corresponding to two charged fragments being produced after dissociation, as has frequently been seen in other molecules, including the dihalomethyl CH_2I_2 [94]. This feature typically presents as a curve originating at high momentum, and decreasing in

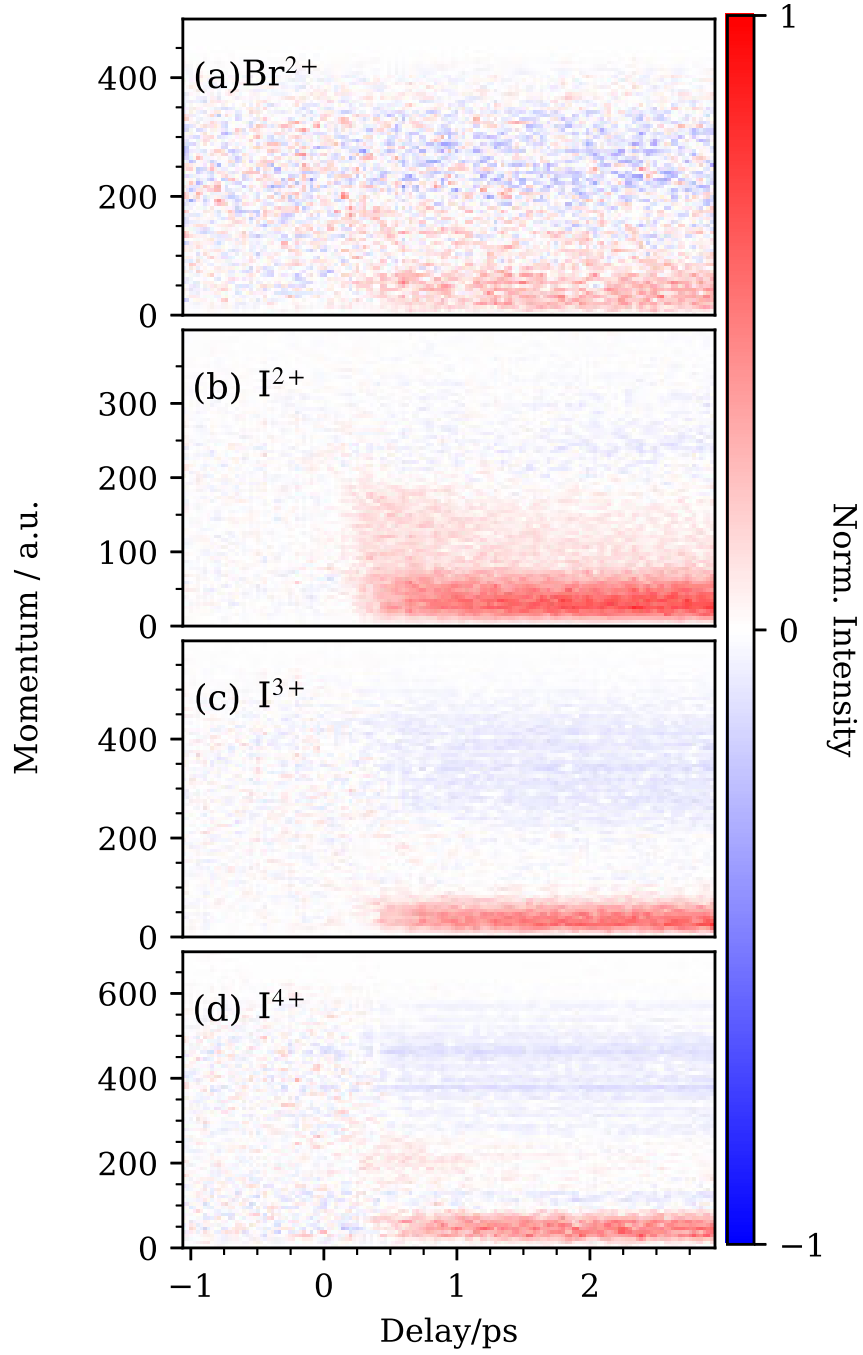


Figure 4.9: Subtracted momentum distributions are produced by removal of any XUV-only signals by subtracting the average of the pre- t_0 intensity. Shown are the ions that exhibit noticeable time-dependence: Br^{2+} , I^{2+} , I^{3+} and I^{4+} .

momentum with increasing delay time. This is due to the separation between the fragments increasing with delay, and hence the Coulombic repulsion between the two fragments decreases, leading to a lower momentum signal. The lack of any clear detection of this feature (with only slight hints visible in the lower charged fragments) is explained by the chosen XUV wavelength used in this experiment (13.1 nm). This wavelength was selected to ionise the iodine 4d orbital, rather than being tuned for the bromine, and so events where both dissociated I and Br are both ionised occur at very low frequency, preventing observation of a Coulomb curve within the statistics recorded here.

The low-momentum channel that occurs after t_0 is the result of an electron migrating from a neutral fragment to stabilise a more positively charged fragment. This process is described in detail in Section 2.5, but in brief, at short separations the charge is able to migrate from a neutral fragment to a highly charged ion, while at longer separations the Coulombic barrier is too great, and stabilisation can no longer occur, resulting in the appearance of the signal. The constant momentum of this channel is due to the lack of Coulombic repulsion, as only one fragment is charged, meaning the only velocity possessed by the fragment is any remaining energy after neutral dissociation. Fitting a Gaussian function to this channel enables measurement of the neutral dissociation velocity of each ion. As there is no Coulombic repulsion, the neutral velocity measured from different charge states of the same atom should be the identical. Therefore, an average of the measured velocities for each ion can be used to give a better approximation of the neutral dissociation velocities. For Br^{2+} , a neutral dissociation energy of 0.18 ± 0.014 eV ($\sigma = 0.128$ eV) was measured, while for iodine the energy was 0.086 ± 0.003 eV ($\sigma = 0.047$ eV) when averaged over I^{2+} and I^{3+} . Converting to velocity gives 664 ± 54 and 367 ± 13 ms^{-1} for bromine and iodine respectively.

Kinetic Energy Partitioning

Using these energies, it is possible to estimate whether these fragments result from a two-body fragmentation into a halogen and halomethyl fragment, or if a

Table 4.2: Energy partitioned into internal modes of the halomethyl fragment for both C-I and C-Br cleavage. D_0 is the relevant C-X dissociation energy. E_{avl} is remaining energy of a 202.5 nm photon after bond dissociation, E_{tot} is the total energy possessed by the halogen and halomethyl fragments and $E_{\%}$ is the percentage energy possessed by the two fragments compared to total available energy.

Channel	D_0	E_{avl} (eV)	E_{tot} (eV)	$E_{\%}$ (%)
$\text{CH}_2\text{Br} + \text{I}$	2.39	3.81	0.2	5.3
$\text{CH}_2\text{I} + \text{Br}$	2.94	3.26	0.31	9.6

three-body fragmentation occurs, producing two halogens and a methyl. Using the known dissociation energies for the C-I and C-Br bonds ($D_0 = 2.389$ and 2.986 eV, respectively), the kinetic energy of the two fragments can be compared to the total available energy. This comparison is shown in Table 4.2, where D_0 is the bond dissociation energy, E_{avl} is the remaining energy after bond dissociation by a 200 nm photon, E_{tot} is the total energy possessed by the halogen and halomethyl fragments, $E_{\%}$ is the percentage energy possessed by the two fragments compared to the total available energy.

The shown value for fragment energy after C-I cleavage in Table 4.2 ($E_{\%}$) is considerably lower for the experimental data measured here, compared to a value recorded by Burt *et al.* in 2017 of 32-34% for a two-body dissociation[19]. While this value was recorded at a different UV wavelength (271.6 nm), Lee *et al.* have shown that the amount of internal excitation is broadly consistent across wavelengths for CH_2BrI [86]. The kinetic energy values measured here would correspond to 90% and 95% of available energy being partitioned into internal modes for C-Br and C-I cleavage respectively, with little remaining for translational energy. An alternative to a two-body dissociation with high internal energy deposition is demonstrated below, where it is found that instead a three-body dissociation occurs, with the majority of the photon energy contributing to C-I and C-Br cleavage.

Charge Transfer Analysis

The above analysis eliminated a two-body fragmentation as a possibility. The fragmentation was further assigned to a three-body process by looking at the onset time of the low-momentum channel. As mentioned above, this channel is the result

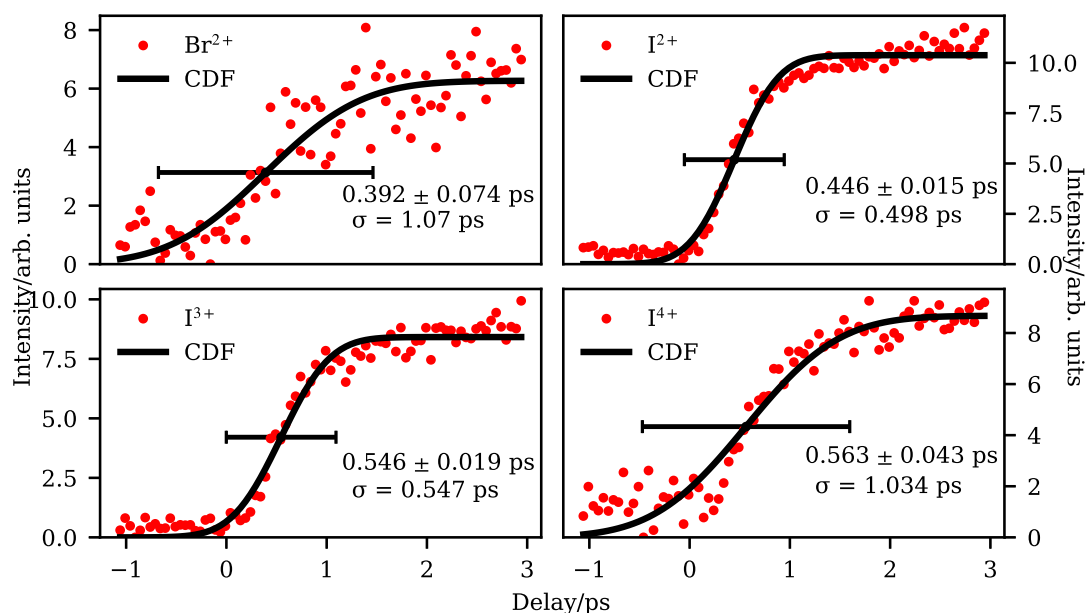


Figure 4.10: Obtained ' t_{crit} ' values from fitting a CDF to the low momentum channel in Br^{2+} and I^{2-4+} . t_{crit} corresponds to the time at which the fragments are sufficiently separated that charge transfer can no longer occur.

of an electron migrating from a neutral fragment to a charged fragment, stabilising the positive charge. The charge transfer channel has a different onset time for each of the ions in Figure 4.9, as the distance (and hence time) at which charge transfer can occur is dependent on the identity of the ion and its charge state. For each of Br^{2+} and I^{2-4+} , the onset time was determined by fitting a CDF to the low-momentum channel. These fits are shown in Figure 4.10, and it can be seen that for Br^{2+} a t_{crit} (which corresponds to the time at which charge transfer is no longer possible) of 0.392 ± 0.074 ps was seen, while for the iodine charge states 2^+-4^+ , t_{crit} values of 0.446 ± 0.015 , 0.546 ± 0.019 and 0.563 ± 0.043 ps were measured respectively.

Using the neutral dissociation velocities obtained above, the separation velocities can be calculated for both the two- and three-body fragmentation pathways. This was done by assuming conservation of momentum and a back-to-back recoil for the two-body event. For the three-body process the separation velocities are more complicated. For each of iodine and bromine, the recoil velocity of CH_2 was calculated using trigonometry to determine the horizontal and vertical components of the velocity for CH_2 recoiling against each halogen respectively. This then

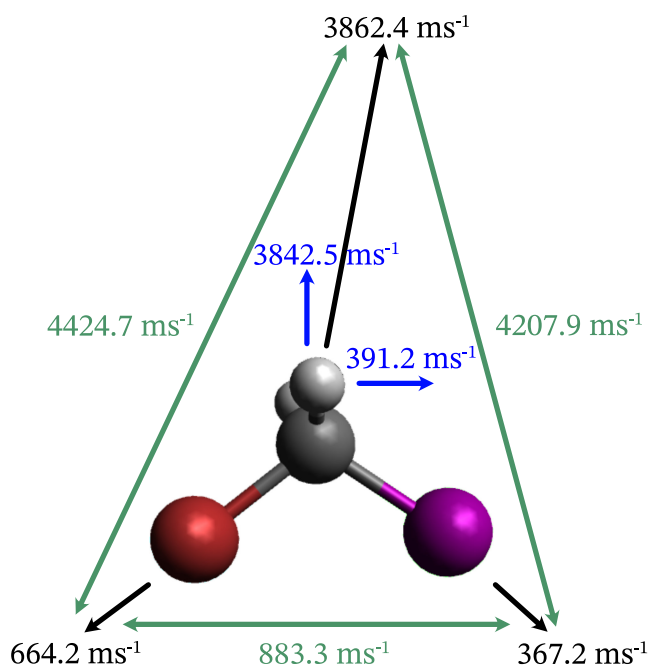


Figure 4.11: Determined velocities of each fragment, and their separation velocities from each other fragment during the three-body dissociation pathway. Black arrows correspond to individual fragment velocities (determined via Gaussian fitting of the low momentum channel for I and Br and via trigonometry for CH_2), blue corresponds to the summed horizontal and vertical velocity components for CH_2 recoiling against Br and I, and green corresponds to the separation velocities of each fragment against the other two.

allowed the total velocity of the CH_2 to be calculated, and hence the separation velocity for it against each halogen, again via trigonometry. A schematic showing the recoil velocity of CH_2 against each halogen, as well as their total velocities and separation velocities is shown in Figure 4.11.

The OTB model described in Section 2.5 can then be used to determine the fragment separation at which charge transfer should theoretically no longer be possible for each of the potential CT pathways, which are, a two-body fragmentation into charged halogen and neutral halomethyl, a three-body fragmentation with charge transfer between a charged halogen and a neutral halogen, and a three-body fragmentation with charge transfer between a charged halogen and a methyl fragment. As the OTB model considers the ionisation potential of the neutral

Table 4.3: Comparison of predicted OTB times at which charge transfer can no longer take place for the three possible neutral dissociation reaction channels of CH_2BrI . X corresponds to the neutral electron donating fragment and Y to the charged electron accepting fragment. OTB R_{crit} and OTB t_{crit} correspond to the distance and time that charge transfer can no longer occur at according to the classical over-the-barrier model, and Exp. t_{crit} is the time charge transfer cannot occur determined from a CDF fit to the experimental data.

	X/Y ^{p+}	v (ms ⁻¹)	OTB R_{crit} (Å)	OTB t_{crit} (ps)	Exp. t_{crit} (ps)
(i)	$\text{CH}_2\text{Br}/\text{I}^{2+}$	860 ± 31	6.40	0.74 ± 0.028	0.45 ± 0.015
	$\text{CH}_2\text{Br}/\text{I}^{3+}$	860 ± 31	7.47	0.86 ± 0.031	0.55 ± 0.019
	$\text{CH}_2\text{Br}/\text{I}^{4+}$	860 ± 31	8.36	0.72 ± 0.035	0.56 ± 0.043
	$\text{CH}_2\text{I}/\text{Br}^{2+}$	1040 ± 85	6.56	0.63 ± 0.052	0.39 ± 0.074
(ii)	Br/I^{2+}	883 ± 333	4.67	0.53 ± 0.20	0.45 ± 0.015
	Br/I^{3+}	883 ± 333	5.44	0.62 ± 0.23	0.55 ± 0.019
	Br/I^{4+}	883 ± 333	6.10	0.69 ± 0.26	0.56 ± 0.043
	I/Br^{2+}	883 ± 333	5.28	0.60 ± 0.23	0.39 ± 0.074
(iii)	$\text{CH}_2/\text{I}^{2+}$	4210 ± 1200	5.33	0.13 ± 0.037	0.45 ± 0.015
	$\text{CH}_2/\text{I}^{3+}$	4210 ± 1200	6.21	0.15 ± 0.043	0.55 ± 0.019
	$\text{CH}_2/\text{I}^{4+}$	4210 ± 1200	6.96	0.17 ± 0.048	0.56 ± 0.043
	$\text{CH}_2/\text{Br}^{2+}$	4420 ± 1200	5.33	0.12 ± 0.033	0.39 ± 0.074

fragment (IP = 8.61, 8.4, 10.35, 11.81 and 10.45 eV for CH_2Br , CH_2I , CH_2 , Br and I respectively), considerably different R_{crit} values are obtained depending on where the charge migrates from. Subsequently, taking the R_{crit} distances obtained by the OTB model, and the fragment separation velocities obtained from the neutral dissociation channel, a theoretical separation time at which charge transfer is no longer possible can be obtained for each ion. This OTB t_{crit} can be compared to the experimental t_{crit} to indicate the most probable charge transfer reaction channel.

Table 4.3 shows the results of these calculations, where the first column indicates the described reaction channel, with X corresponding to the neutral, electron donating fragment, and Y corresponding to the charged, electron accepting fragment.

Comparing the values in sections (i) and (ii) of Table 4.3, which show charge transfer between a neutral halomethyl and charged halogen, and a neutral halogen and charged halogen respectively, there is a stronger agreement between the three-body pathway compared to the two, further confirming the earlier assignment of dissociation occurring via a three-body mechanism, found from looking at the

kinetic energy partitioning. Comparing sections two and three in Table 4.3 shows that in the three-body dissociation, the charge migrates from a neutral halogen rather than a neutral methyl fragment, with much greater agreement measured for the halogen transfer pathway. The OTB model predicts a far shorter t_{crit} for the methyl pathway than is observed experimentally, which is a consequence of the much lower mass of a methyl fragment compared to bromine or iodine, leading to a large separation velocity, and hence shorter time to reach R_{crit} . The different timescales in the dissociation of a C-I versus C-Br bond, as well as the different masses of iodine and bromine mean that the bond cleavages are unlikely to be completely concerted, with some small degree of asynchronicity. However, the delay between the two dissociations is likely to be small, as a fully sequential dissociation would result in significantly less velocity being imparted to the second halogen, due to greater rotational excitation of the halomethyl fragment. Unfortunately this could not be experimentally verified here as the XUV wavelength was tuned to primarily ionise the iodine, resulting in insufficient statistics where both iodine and bromine were charged, and therefore preventing time-dependent covariance analysis.

4.4 Summary

In this Chapter time-independent Coulomb explosion imaging was used to determine the location of molecular charge after interaction with an XUV pulse. Recoil-frame covariance analysis determined that for events where a three-body explosion occurred, there are situations where all three fragments are charged, and also events where the methyl fragment remains neutral. This was seen as a broad signal spread off-180°, and also as a more intense signal at 180°. Evidence was also seen of a two-body explosion into a halogen and halomethyl fragment. For this explosion, the charge on the halomethyl was found to reside primarily on the halogen as opposed to the carbon.

The time-dependent Coulomb explosion imaging data was used to follow the photodissociation of CH₂BrI at 202.5 nm. The constant, low momentum neutral dissociation feature present in all multiply charged halogens was used to characterise

whether the dissociation proceeded via a two- or three-body mechanism. This was accomplished by first using the fragment velocity to determine the percentage of available energy partitioned into kinetic energy, and then comparison of that value to previously measured data for the two-body dissociation. This was supported by comparison of the varying onset time of this neutral channel to an OTB model. The combination of these two measurements allowed the dissociation mechanism to be assigned as three-body, and for the location of the charge in the charge transfer reaction to be identified as coming from a neutral halogen fragment rather than a methyl.

Both the time-independent and time-dependent data in this Chapter highlight multiple different capabilities of CEI to characterise experimental data. The time-independent study demonstrates that the kinetic energy information obtained from the XUV-only data can be used to identify which atom in the molecule is charged after interaction with the laser. This has the potential in future studies to help disentangle the origin of signals where a molecule possesses multiple different atoms that are easily ionised by an FEL. The time-dependent data demonstrates that the low-momentum charge transfer channels can be compared to an over-the-barrier model to determine whether fragments are produced via a two- or three-body dissociation, and in the case where a three-body dissociation does occur, demonstrates that analysis of the charge transfer dynamics allows which fragments the charge migrates from to be determined. This has potential in future studies to allow easy characterisation of the primary dissociation products in molecules where there is enough excitation energy to dissociate multiple bonds.

5

Characterising the Overlapping Dissociation Channels of C₆H₅I

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5.1 Background

The previous Chapter shows how CEI can be used to identify whether a photodissociation proceeds via a two- or three-body route. For molecules where there are multiple overlapping accessible excited states, and hence multiple different dissociation mechanisms that can occur, CEI has previously been used to distinguish two different mechanisms which lead to a ground and excited iodine photoproduct, and also to interpret multiple overlapping dissociations[18]. Here, CEI, coupled with

analysis of the data produced when a sole atom is charged, is used to characterise the 200 nm photodissociation dynamics of iodobenzene, a molecule which is known to possess complicated photochemistry and undergo multiple different dissociation routes. This serves two purposes: firstly, it furthers our understanding of the photodissociation dynamics of iodobenzene, and secondly, it provides additional evidence as to CEI’s suitability to characterise such dynamics, by identifying multiple properties of the overlapping channels, including the amount of energy partitioned into internal modes, a dissociation branching ratio, and the excited state of the cofragment, the latter of which has previously not been accomplished before in a CEI experiment.

Iodobenzene possesses a large number of UV absorption bands, labelled A-F, which have absorption maxima centred at 256 nm for the A-band, and 164 nm for the F-band, with the remaining bands lying between this range. There has been a large amount of prior investigation at longer wavelengths, to probe the A- and B-bands, but significantly less for shorter wavelengths. The dynamics of the dissociations dramatically change with decreasing wavelength, due to multiple higher energy excited states becoming accessible.

At longer wavelengths, within the A-band and higher edge of the B-band, two dissociation channels have been observed. Simple halogenated molecules, such as halo-alkyls, primarily undergo dissociation after a $n \rightarrow \sigma^*$ excitation. A similar process occurs in iodobenzene, and corresponds to a rapid, direct dissociation. In addition to this direct dissociation, a slower indirect route has also been measured. In iodobenzene, due to the presence of the phenyl (Ph) ring, the (n, σ^*) transition of the C-I bond overlaps with the (π, π^*) transition of the phenyl ring. This overlap results in a significant portion of the excitation energy being partitioned into the internal modes of the ring, and causes iodobenzene to adopt a pre-dissociative state[95–100]. Both of these channels have been found to possess routes that lead to both ground, I, and excited, I*, photoproducts, which results in the detection of four different velocity distributions. As the wavelength decreases from the low-energy A-band to deeper within the B-band, the proportion of I* photoproducts

increases. Within this longer wavelength range, the parameters associated with the dissociation have been reasonably well documented. At 266 and 248 nm respectively, 30% and 43% of the energy available following absorption was partitioned into the internal modes of the phenyl ring for the direct dissociation, and at 266 nm 74% of available energy was partitioned into internal modes of the phenyl ring for the indirect dissociation. Additionally, the two dissociations were found to have a branching ratio of direct:indirect of 84%:16% at 266 nm[101, 102].

Sage *et al.* completed a thorough investigation of the A- and B-band dynamics (306-206 nm), and extensively described the excited states involved at these wavelengths. As mentioned above, four different dissociation channels were observed: two channels from the I photoproduct, and two channels from the I* photoproduct, each with their own distinct velocities. For the I photoproduct, the lower velocity channel of the two was assigned to excitation to a bound $\pi\pi^*$ state that subsequently couples to a dissociative state. In this channel, greater internal energy deposition occurred, resulting in less fragment kinetic energy. The intensity of this signal grew as the wavelength decreased, as additional $\pi\pi^*$ states (e.g. $3B_1$, $4B_1$ and $3B_2$) are accessible with higher energy excitation photons. The higher velocity channel had a simpler origin, and was assigned mainly to an $n/\pi \rightarrow \sigma^*$ transition to the $2A_1$ state, with some minor contribution from the $2B_1/2B_2$ states. For the I* photoproducts, initially one dissociation was observed. At long wavelengths this was assigned to an $n \rightarrow \sigma^*$ transition to the $4A_1$ state, similar to the higher velocity signal in the I photoproduct channels. With shorter wavelengths, initial excitation was to the $5A_1$ state, and so the origin of this signal was assigned to rapid predissociation of $5A_1$ to $4A_1$, with dissociation then proceeding in the same manner as with the longer wavelengths. A second strong dissociation channel only appeared in the I* distributions when the excitation wavelength was between 206 and 220 nm. Within this range, a second narrow feature appears at a higher velocity, with growing intensity with decreasing wavelength. This feature was attributed to excitation of high-lying levels of the $5A_1$ state, followed by coupling to the $7A_2$ and $8B_2$ states. It was determined that crossing to these states was only possible from high lying

levels of the $5A_1$ state as the $5A_1$ state can first be accessed at ~ 230 nm, and yet the feature does not appear until < 220 nm[97].

There has been far less analysis of the excitation dynamics at shorter wavelengths, with little characterisation of the parameters involved in the dissociations. One study that has been carried out was a probing of the dynamics at 200 nm by Hu *et al.*, centrally within iodobenzene’s C-band, akin to the wavelength utilised for data collection within this Chapter. Unlike at the longer wavelengths, where four dissociation channels were observed, Hu *et al.*’s simulated PECs found that only three dissociations were possible, and in fact they only experimentally observed two. Hu *et al.* found that initial excitation of iodobenzene populated the $7B_1$ and $7B_2$ excited states, which both progressed in a similar manner. These states are inaccessible at 206 nm, the lowest wavelength studied by Sage *et al.* on the edge of the B-band, and so a difference in dynamics is to be expected. After excitation to the $7B_1/7B_2$ states, three states are accessible. The simplest occurs due to overlap with the $5B_2$ state, where the molecule subsequently dissociates to give electronic ground-state Ph(X) and ground-state $I(^2P_{3/2})$ photoproducts. However, despite theoretically being accessible, no experimental evidence of this channel was detected by Hu *et al.* and this was attributed to the much slower timescale of the predominantly triplet $7B_1/7B_2$ states transitioning to the predominantly singlet $5B_2$ state, in comparison to rapid relaxation to other accessible states. As such, it was determined this channel occurred in undetectable quantities. Alternatively to crossing to the $5B_2$ state, rapid crossing from the $7B_1/7B_2$ states to the $7A_1$ and $8B_2$ states was observed. The excited molecule can then either remain on these high energy $7A_1/8B_2$ states and dissociate to give the electronically excited Ph(A) and ground-state $I(^2P_{3/2})$ photoproducts, or a second crossing can rapidly occur, and the molecule subsequently reaches any of the $7B_2$, $8A_2$ and $8B_1$ states, where dissociation produces electronic ground-state Ph(X) and spin-orbit excited $I(^2P_{1/2})$ photoproducts[103]. Therefore Hu *et al.* concluded that, at a dissociation wavelength of 200 nm, two different dissociation channels can occur.

As mentioned above, the excitation wavelength utilised within this Chapter was 200 nm, the same as used by Hu *et al.* Therefore, it was expected the observed dissociation dynamics here would follow similar routes to those posited by Hu *et al.* Using a 200 nm pump-10.3 nm probe setup, these dissociation routes are followed, their parameters characterised, and the cofragments to the dissociation determined. Supporting evidence is also provided, obtained via a 200 nm pump-800 nm probe setup.

Figure 5.1 shows the expected time-dependent CEI channels at this pump/probe wavelength. After dissociation, there are two different pathways that can occur when interacting with the probe pulse. Firstly, the resultant fragments can both become charged and Coulombically repel. Secondly, if only the iodine is ionised, at short separations a charge transfer event can occur (Section 2.5), producing two charged fragments, while at longer separations the barrier to electron transfer is too high, and the cofragment remains neutral, with both fragments only possessing any energy remaining after dissociation and internal energy partitioning.

5.2 Experimental

5.2.1 Experimental Setup - UV/XUV

The initial experiment was carried out at the SACLA facility in Japan and utilised a 200 nm UV pump pulse, and a 10.3 nm XUV probe pulse to collect data[105]. References [106] and [55] detail the specifics of the two laser systems, but a short summary of their operation is as follows. The fourth harmonic of a 10 mJ, 40 fs, 800 nm IR pulse was used to generate the 200 nm pulse. This 800 nm laser system consisted of a mode-locked oscillator (Vitara, Coherent Inc.), a chirped pulse amplification system (Legend Elite, Coherent Inc.) and a home-built multi-pass amplifier. Unfortunately a precise measurement of the UV pulse duration was not taken during the experiment, however it is estimated to be not more than 200 fs (and likely lower). This gives a minimum UV intensity of $1.6 \times 10^{11} \text{ W cm}^{-2}$ (taking a pulse energy of 1 μJ and a focal spot size of 88 μm). Note that this is the minimum intensity, and it is likely higher than this value.

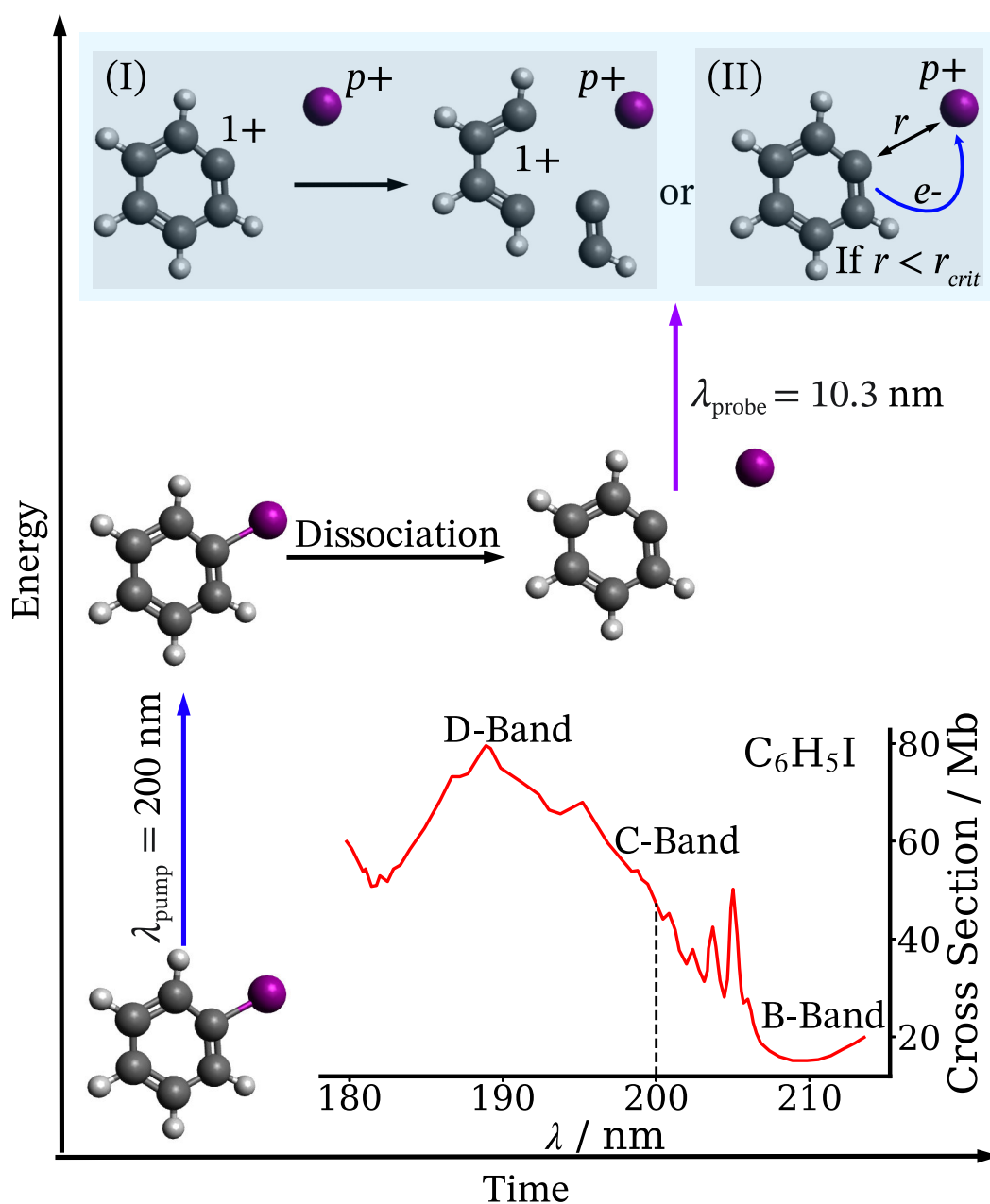


Figure 5.1: Schematic of the primary pump-probe reactions accessible to iodobenzene at 200 nm (shown with a dashed line on the absorption spectrum). Two different dissociation mechanisms can occur after interaction with the pump pulse. After interaction with the probe pulse, these can be detected either through channel (I), where both the iodine and phenyl fragments can become charged and Coulombically repel, with the phenyl fragment subsequently further fragmenting. Note that here only one possible fragmentation of the phenyl ring is shown in (I). Alternatively, channel (II) can be detected, where only the iodine fragment is charged. In this case a charge transfer process can occur depending on the separation of the two fragments (as described in Section 2.5). The UV absorption spectrum was adapted from Palmer *et al.*[104].

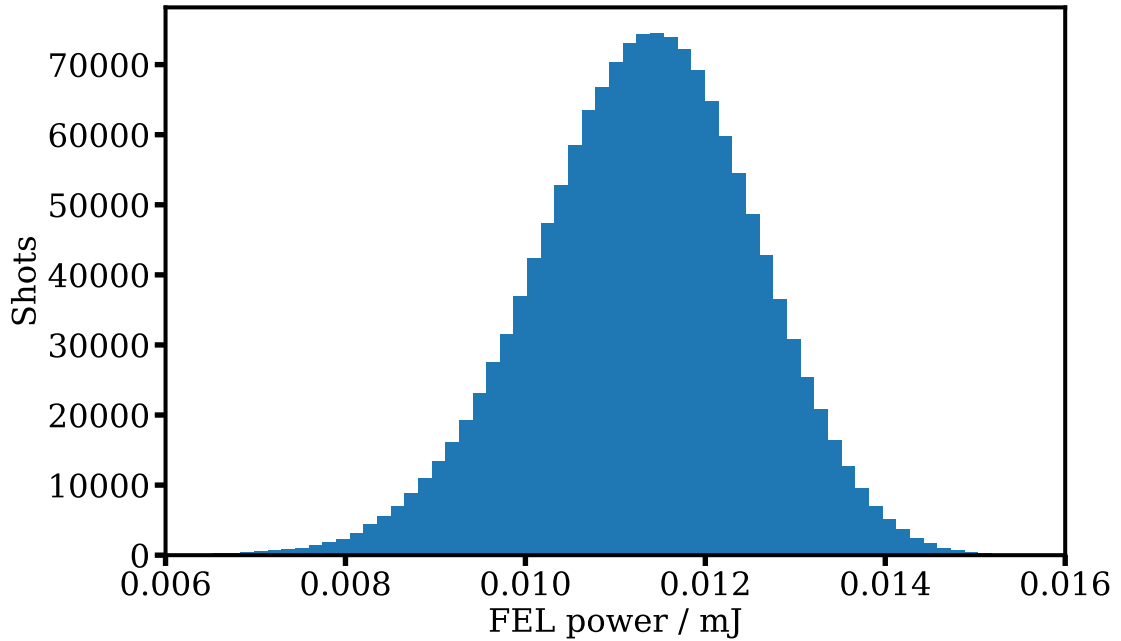


Figure 5.2: Histogram of FEL pulse energies recorded throughout the experiment.

A 10.3 nm probe pulse was used, and intersected the interaction region perpendicular to the molecular beam. This wavelength was chosen to site-selectively ionise iodine at the 4d edge. The absorption cross-sections of the I, C and H atoms are approximately 1.4 Mb, 0.1 Mb and 0.01 Mb respectively, indicating that iodine will be ionised at a significantly greater frequency[87, 107]. The full FEL energy distribution measured during this experiment is shown in Figure 5.2, and had an average energy of 11.4 μ J. After passing through a 0.65 μ m zirconium filter, and accounting for various losses along the beamline, an interaction region energy of 1.33 ± 0.13 μ J was recorded. Using the known focal spot size and pulse duration of 10 μ m and 30 fs respectively, a probe intensity of $1.1 \pm 0.1 \times 10^{14}$ W cm $^{-2}$ was calculated.

A computer controlled optical delay stage was used to vary the time between the pump and probe pulses, with data being recorded in 50 fs steps. The zero delay, t_0 , was estimated using the onset of the I^{2+} Coulomb curve. A Coulomb curve is caused by two charged dissociated fragments recoiling against one-another, and so the earliest point at which this curve is detected is the earliest point at which the molecule has been dissociated and subsequently ionised. That is, the earliest point

at which the pump pulse arrived before the probe pulse. A very short delay before this point will therefore be the point at which the two pulses are overlapped, and this point is likely within the 50 fs resolution of the experiment.

A pulsed supersonic molecular beam was used to introduce the sample into the interaction region. Ion optics with velocity mapping potentials directed ions along the ToF tube, where they were recorded by a dual MCP setup, along with a hexanode delay-line detector. The positional and temporal information of these ions was recorded (x,y,t) for each hit, giving accurate momentum data for each ion[108].

5.2.2 Experimental Setup - UV/IR

The UV/XUV data presented in this Chapter was supported by additional measurements taken using a UV/IR pump-probe system. Here, a 200 nm pump pulse was generated by a TOPAS system and an 800 nm probe pulse was generated by a Spectra-Physics Solstice Ace laser system (both described in detail in Section 3). The Solstice produced 800 nm, 1 kHz, 5 W compressed laser pulses, a proportion of which were redirected into the TOPAS to generate the UV pulse, with the remainder being used as the probe pulse.

A Frequency-Resolved Optical Gating (FROG) autocorrelator was used to determine the 800 nm pulse duration. This autocorrelator uses a beam splitter to separate the 800 nm pulse. One beam is passed directly to a concave mirror and directed through a β -BBO crystal (which is used as the non-linear optical medium). The second is reflected onto a delay stage and then again directed through the β -BBO. The pulses overlap within the BBO and produce the second harmonic with a wavelength of 400 nm. The intensity of this second harmonic is then recorded by a spectrometer (this setup is shown schematically for our experiment in Figure 5.3).

The delay between the initial two pulses was varied, and a measurement of the intensity of the second harmonic recorded at each delay. Plotting this as intensity against delay allows the FWHM, and subsequently the pulse duration, of the initial laser to be extracted. In this experiment, a pulse duration of 47 ± 2 fs was determined, and this measurement is shown in Figure 5.4. An anti-reflective

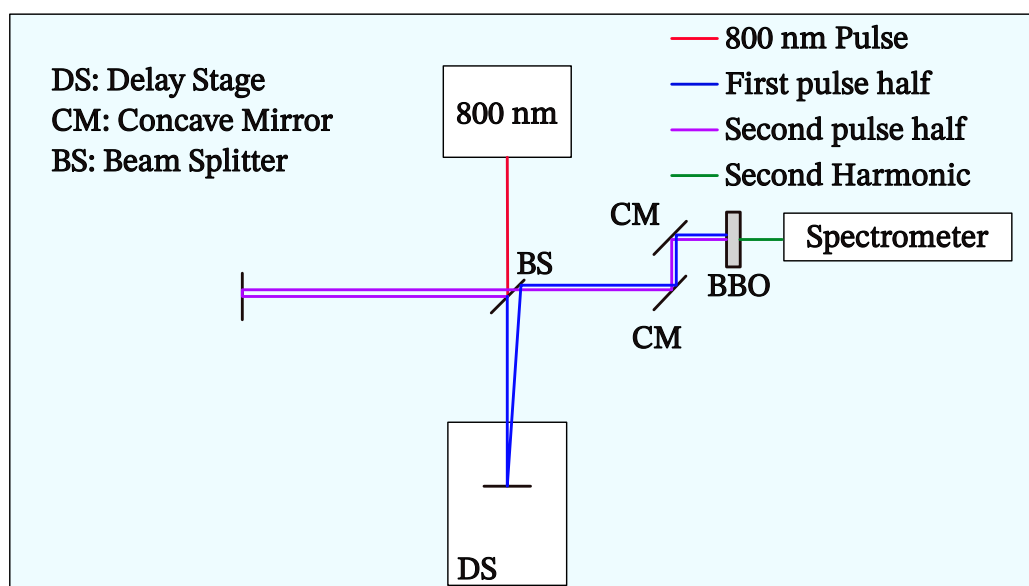


Figure 5.3: Schematic representation of the FROG autocorrelator used to characterise the pulse duration of the 800 nm probe pulse.

(660-1380 nm) focusing lens was used to focus the IR pulse into the centre of the interaction region. The laser spot size was measured as 7 mm prior to the lens, which, taking a focal length of 35 cm, gave a focal spot size of 60.4 μm . When measured at 200 Hz, after losses along the beamline and wave-plate attenuation, the IR power was recorded as 47 mW, giving a peak probe pulse intensity of $3.5 \pm 0.15 \times 10^{14} \text{ W cm}^{-2}$. The 200 nm pulse was emitted from the TOPAS with an average power of ~ 7 mW, and was focused into the centre of the interaction region via an uncoated focusing lens with a focal length of 42.7 cm. As mentioned in Chapter 3, Figure 3.4 shows a schematic of the laser table setup utilised in this experiment.

The sample of gaseous iodobenzene, made up with a helium carrier gas, was introduced into the reaction chamber via a pulsed molecular beam, which intersected the two laser pulses perpendicularly. Positional overlap of the two pulses was achieved by looking at sample ion images in spatial imaging mode, where ion signals show up as a horizontal line, allowing data to be recorded for each pulse, and then horizontally shifted until overlapped. Similarly, focal overlap was achieved by

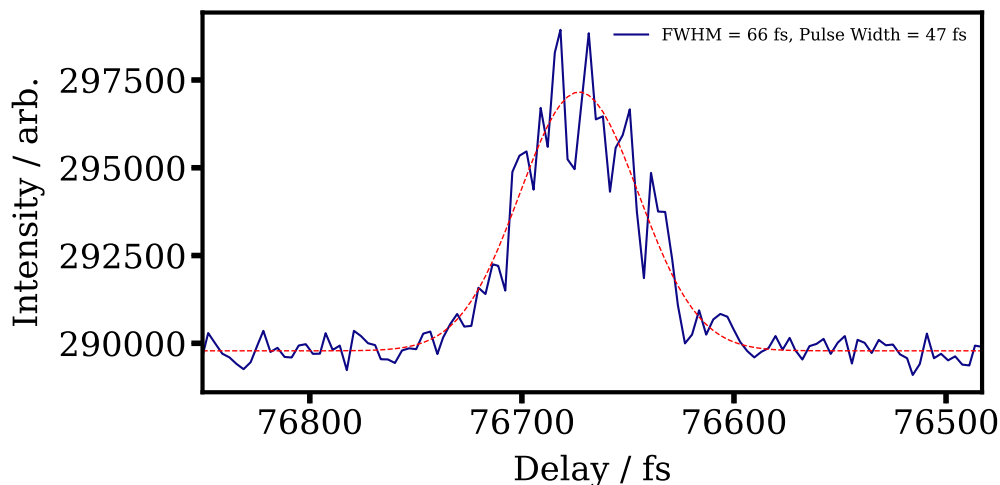


Figure 5.4: Pulse duration of the 800 nm IR laser pulse used in this thesis, determined via Gaussian fitting to the output of an autocorrelator.

looking at the spatial output, with a unidirectional translation stage adjusting the lens positions until the focus was located in the centre of the VMI region.

The temporal overlap of the two pulses, t_0 , was determined by looking for an enhancement in the ion images of iodobenzene. When looking at the ion images, a signal enhancement appeared in the centre of the image when the UV pulse preceded the IR, but was absent when it followed. Data were recorded at both extremes of the delay stage to search for this enhancement, with the positions gradually being shrunk to shorter separations to narrow down t_0 . Figure 5.5 shows four ion images used in obtaining the final position of t_0 , with no enhancement seen in the early image, then a faint enhancement appearing at 50.35 mm that grows in intensity at greater stage distances (which corresponds to later IR).

After ionisation, fragments were directed along a ToF tube by a four-plate ion optic setup, consisting of repeller, extractor, lens and ground plates. These were run under VMI conditions. For our experimental setup two sets of VMI voltages were used, to allow different levels of zoom on the fragments to better isolate signals from lower and higher charged ions. These voltages were 4000, 3510, 2422 and 0 V for the ‘zoomed in’ data and 9000, 7896, 5449 and 0 V for the ‘zoomed out’ data, respectively. The fragments interact with a detector made up of a P47 phosphor screen and two MCPs. The screen was run at 5500 V, the ‘inner’ MCP at 0 V, and the ‘back’ MCP

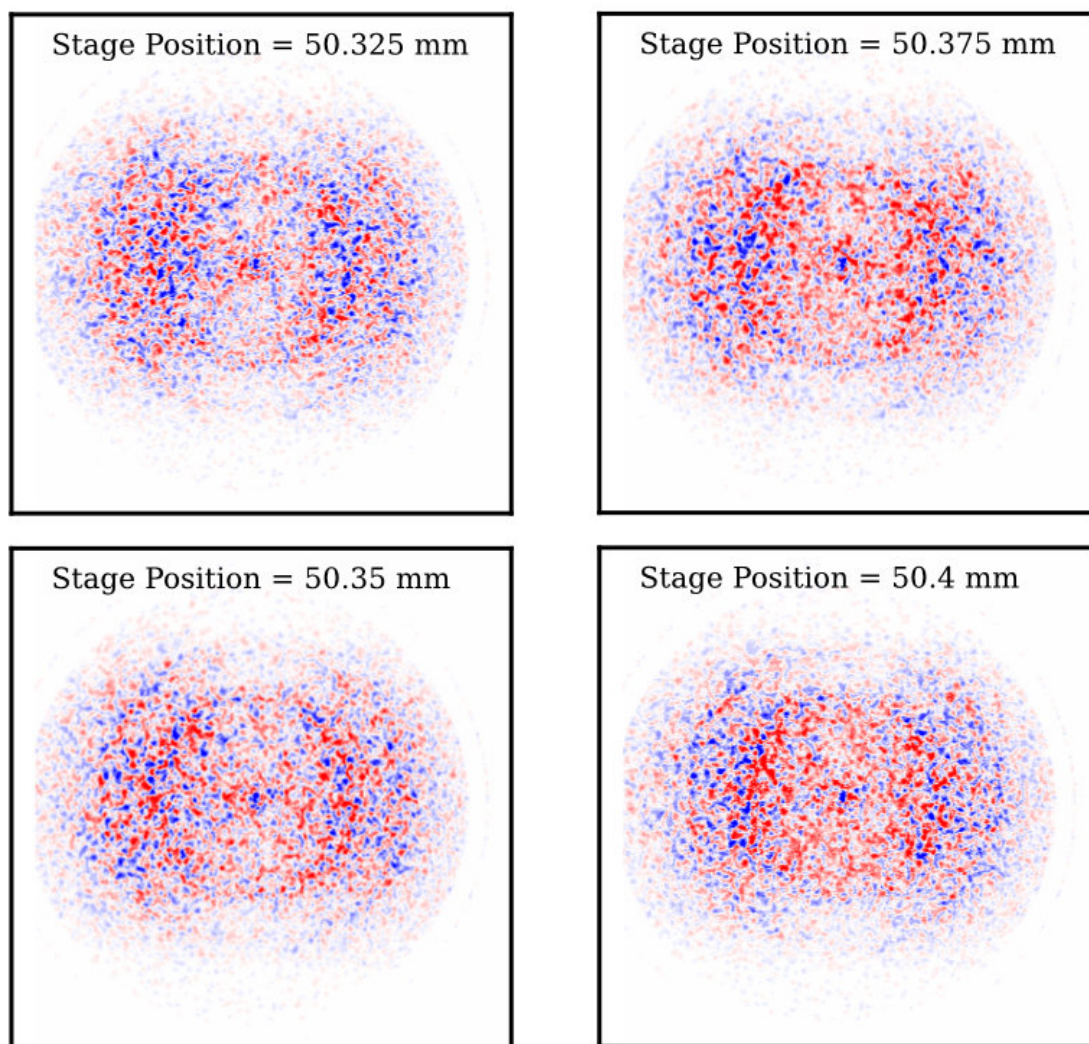


Figure 5.5: Iodobenzene ion images used for obtaining the temporal overlap of the two pulses. A central enhancement appears when the UV pulse arrives before the IR pulse.

at 800 V, which provided a good balance of high hit detection, without causing any long term deterioration of the detector. To allow the experiments to be run at higher IR power and gas pressure without damaging the detector, a Photek GM-MCP3 gating unit was used to gate out high intensity light fragments, with any fragments with a mass of less than or equal to water being gated. This unit operated by keeping the back MCP at 800 V (or low enough that there is no significant activation) when the light fragments collide, and then temporarily pulses the voltage up to 1800 V at later times when heavier fragments would interact.

Hits on the detector were monitored by a PImMS camera (Section 3.3.2), with

a PImMS2 sensor, which recorded the positional and temporal information for each hit. As in the previous chapter, a centroiding process was applied to account for multiple pixel activation by a single photon, as described by Slater[70]. The Solstice was operated at a frequency of 200 Hz, however, due to the limitations of the camera a frequency modulator was used to downclock the trigger of the PImMS camera to an acquisition rate of 20 Hz.

5.3 Results and Discussion - UV/XUV

This section will discuss the dynamics observed from data collected with the UV/XUV experimental setup at SACLA, with a later section handling the UV/IR analysis. Figure 5.6 shows the mass spectra for iodobenzene under two conditions: where the UV pulse arrives after the XUV (labelled UV late), and hence observed fragments are the result of interaction with the XUV pulse only (and to a minor extent XUV-pump/UV-probe interactions); and where the UV pulse arrives before the XUV (labelled UV early) and UV excitation dynamics are observed. Iodine charge states from I^{1-6+} and phenyl fragments of the form $C_yH_x^+$ (where $y = 1-6$ and $x = 1-5$) were detected. It can immediately be seen that while there is negligible difference between the signals seen from the singly-charged ions, for the multiply charged iodine ions an increase in intensity is visible when the UV precedes the XUV pulse, suggesting the presence of time-dependent dynamics. It can be seen that several of the high charged iodine species overlap in m/z with various carbon fragments, complicating the investigation of the dynamics, and this is expanded upon in greater detail below. Similar to the previous chapter, the time-independent results will be presented first, followed by the more relevant time-dependent dynamics.

5.3.1 Time-Independent Data

Therefore, starting with the UV-late data, 3D momentum distributions were produced for all ions observed in the mass spectrum, and these are shown in Figure 5.7. It is worth noting that multiple hydrogens can be lost from each carbon containing fragment, and therefore while the carbon number for each momentum

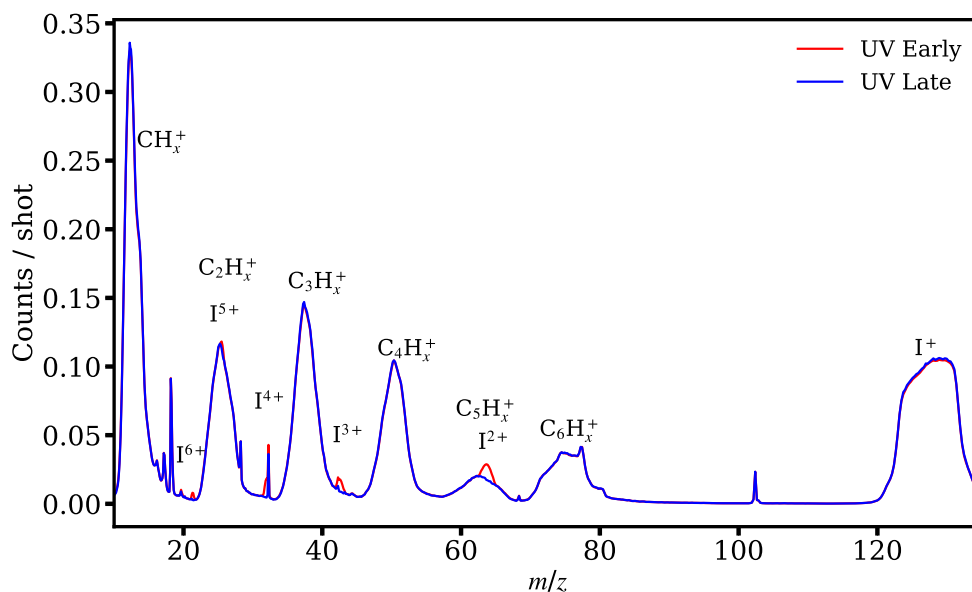


Figure 5.6: Iodobenzene mass spectra for the UV early and UV late events. Parent peak is excluded.

distribution is accurate, the distribution will likely include signal from fragments with varying numbers of hydrogens that overlap within the mass spectra. It is also worth noting the close m/z of $C_5H_5^+$ and I^{2+} , which results in some time-dependent signal appearing in the carbon fragment, that likely originates from the iodine. From these momentum distributions it was determined that all phenyl fragments possess a large time-independent signal, suggesting multiple fragmentation routes for the C_6H_5 molecule. This large number of fragmentation pathways was further confirmed by looking at the ToF-ToF covariance image (Section 3.4.5) shown in Figure 5.8. This was produced using contingent covariance (Section 3.4.4), using ten FEL energy bins.

The strong signal at each ion intersection shows that every ion is covariant with every other ion, and confirms that, for the time-independent data, the charged parent molecule can fragment in many different ways, producing a large combination of charged carbon and iodine fragments, with the highest intensity signal seen between singly-charged iodine ions and singly-charged carbon cofragments.

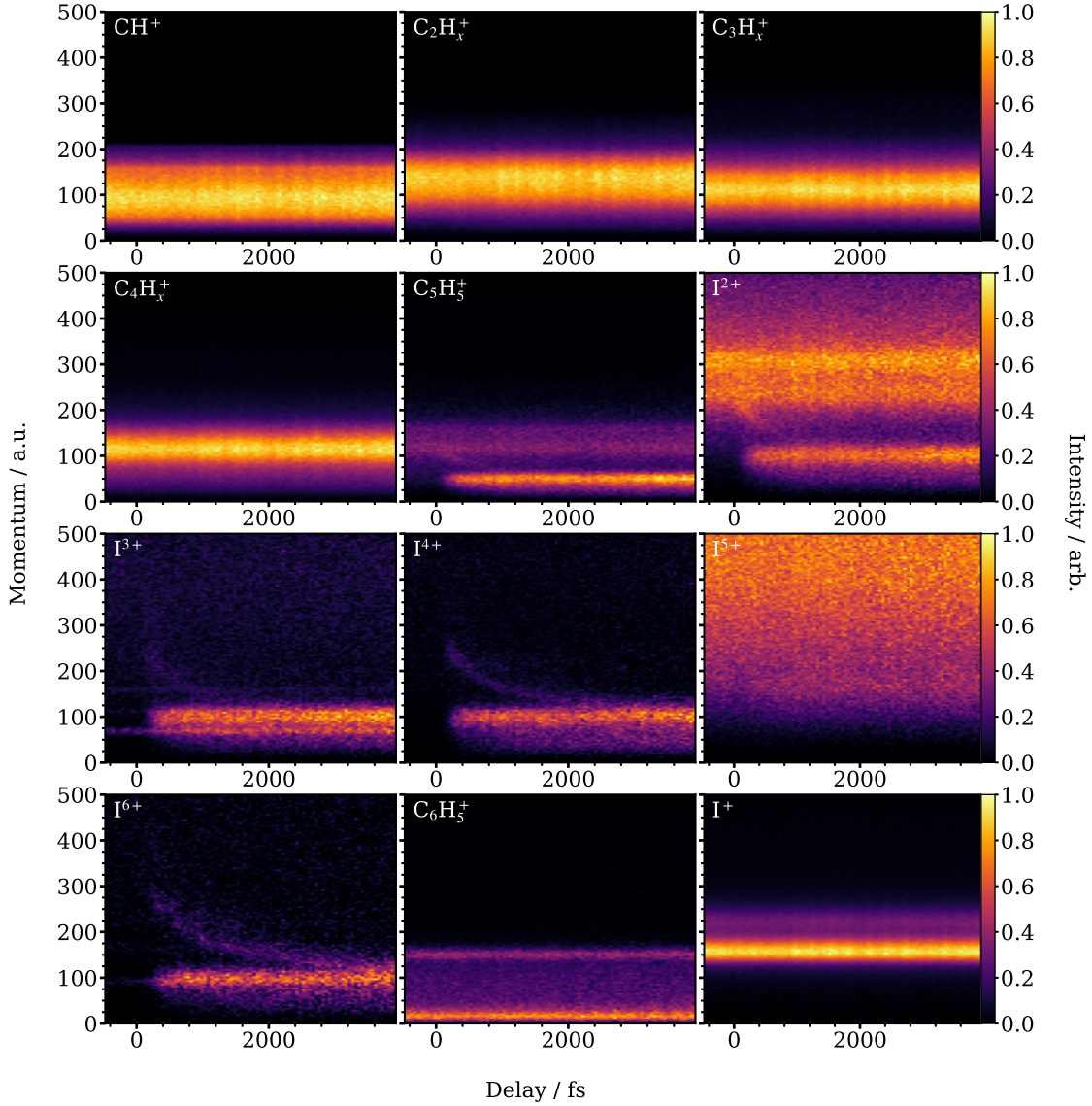


Figure 5.7: Unsubtracted momentum distributions for I^{1-6+} and $C_yH_x^+$ (where $y = 1-6$ and $x = 1-5$).

5.3.2 Time-Dependent Data

Turning to the time-dependent data, signal was enhanced by subtracting off an average of the UV-late signal pre- t_0 . This gave five ions that exhibited time-dependence in their momentum distributions, namely I^{2-6+} . Due to the large overlap between I^{5+} and $C_2H_x^+$, as well as the relatively low statistics of the highly charged iodine signals, I^{5+} was excluded from the following analysis. While I^{2+} also overlaps with a carbon fragment, $C_5H_5^+$, the I^{2+} ions were produced in great enough quantity that a strong signal was still observed. The momentum distributions

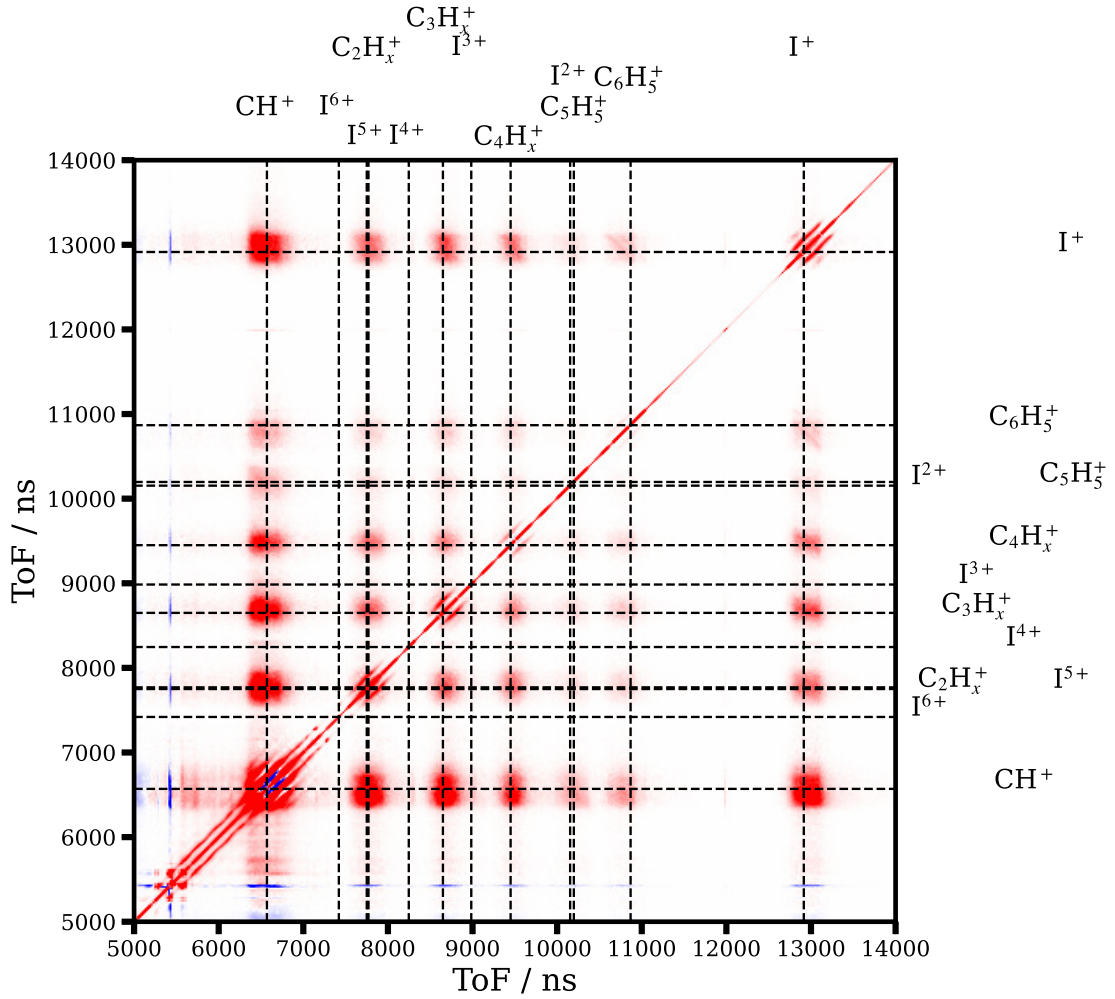


Figure 5.8: ToF covariance image for the time-independent signals seen from iodobenzene, filtering for XUV-early data. Dashed lines match signal to ion labels around the edges of the plot.

for the $I^{2/3/4/6+}$ ions are shown in Figure 5.9.

Three enhancements are visible in each of the ions in Figure 5.9: a Coulomb curve starting at high momentum and decreasing to lower momentum that is assigned to the charged iodine recoiling against another charged cofragment, and two features at low constant momentum, which result from the charged iodine recoiling against neutral fragments. These are labelled using $(p+, q+)$ notation in Figure 5.9 (for I^{2+} only), where p corresponds to the charge on the iodine ion and q denotes the charge on the cofragment. Unusually, no time-dependence was observed in any of the momentum distributions of any carbon containing fragments.

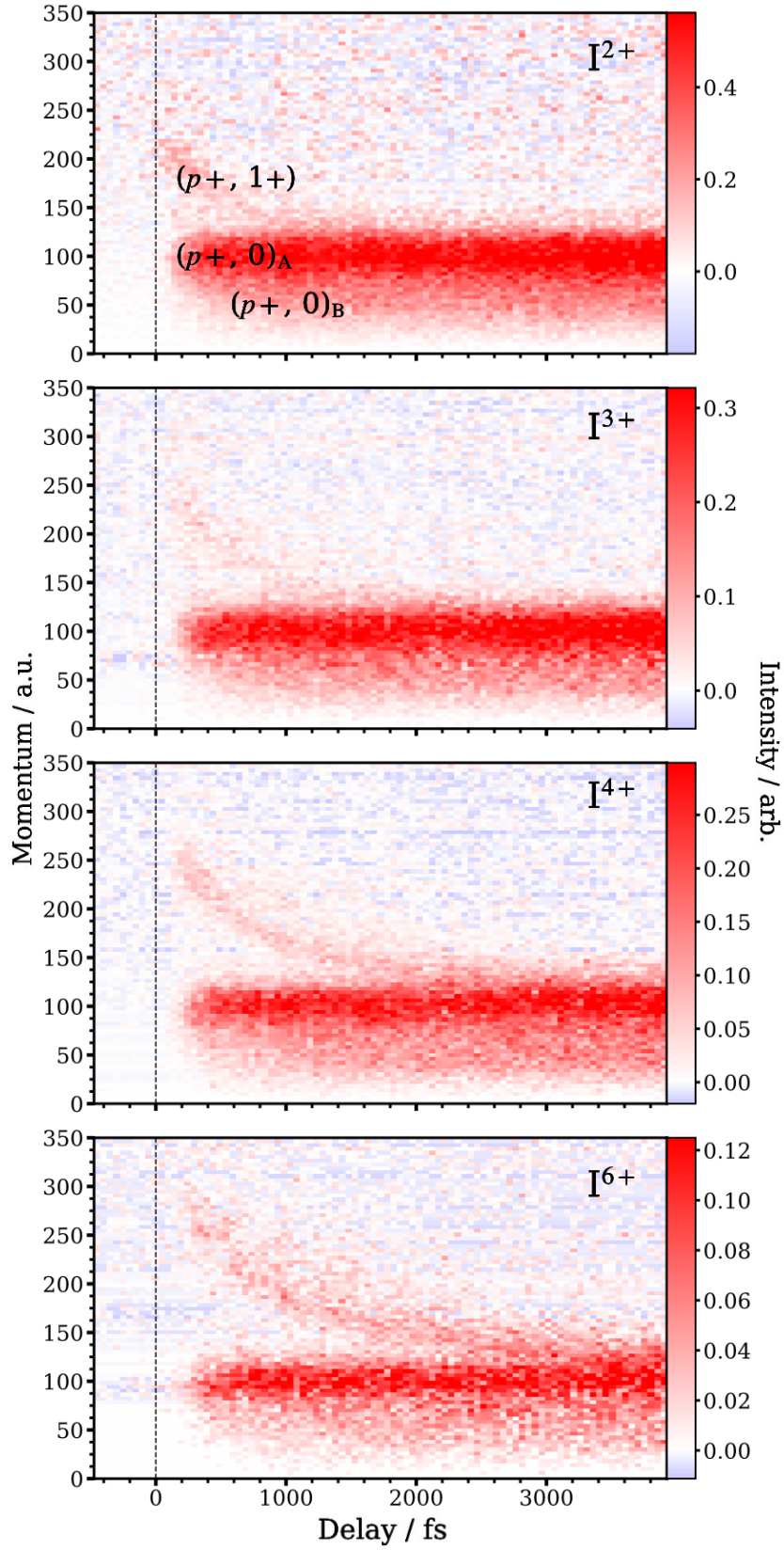


Figure 5.9: Time-dependent background-subtracted momentum distributions for $I^{2/3/4/6+}$. Three enhancements are visible: a Coulomb curve, and two separate constant momentum channels.

This is surprising, as for a Coulomb curve to exist, the ion must be recoiling against another charged species. This lack of time-dependence in the carbon fragments was confirmed by a lack of signal seen in any time-dependent covariance analysis. Therefore, from the UV/XUV data, the cofragment to dissociation can only be inferred (and such an analysis is given below), rather than directly observed. Direct confirmation of the cofragment will be later seen through the UV/IR data. The time-dependent discussion is split into two sections, looking at the $(p+, 0)$ and $(p+, 1+)$ channels respectively.

$(p+, 0)$ Channels

As mentioned above, the low and constant momentum channels are the result of a neutral dissociation process, where there is no Coulombic repulsion and the iodine ions only possess the remaining energy after dissociation and partitioning into the internal modes of the phenyl ring. The existence of two low momentum channels with different onset times implies the occurrence of two different dissociation mechanisms, consistent with the previous work of Hu *et al.* From the simulated PECs reported by Hu *et al.*, and as described above, the two dissociations correspond to the production of a low energy channel with $Ph(X) + I^*$ photoproducts, and a high energy channel corresponding to $Ph(A) + I$ photoproducts. As an excited state having high energy results in less energy available to be converted to kinetic energy, the $Ph(X) + I^*$ channel can be assigned to the $(p+, 0)_A$ channel in Figure 5.9, and the $Ph(A) + I$ channel can be assigned to $(p+, 0)_B$ [103]. Multiple parameters relating to the dissociation mechanisms can be extracted from these neutral channels, namely, internal energy deposition, branching ratios and the excited state of the cofragment.

A global fitting method was used to interpret these low-momentum channels. This global fitting method was developed by Razmus *et al.* and uses three basis functions that can be combined to account for the full $(p+, 0)$ dissociation process[109]. These three basis functions correspond to the three events that occur within the low-momentum region of the momentum distribution: one each for each of the two dissociation channels, and one that corresponds to the ground state

depletion. It is simple to obtain the basis function for the depletion, as pre- t_0 the only occurring event is probing of the ground state molecule, and so averaging this data produces the basis function for the ground state depletion. The other two basis functions are slightly more complicated to isolate due to their overlapping nature, and also the presence of some ground state depletion at low momenta. As the depletion slightly overlaps with the $(p+, 0)$ channels, the intensity of the depletion basis function was manually scaled to avoid over-accounting for the ground state. The scaling was decided based on looking at the high momentum depletion signal, and scaling the intensity of that to zero. After applying the scaling, the other two basis functions still needed to be isolated from the overlapping channels. Filtering the momentum distributions to short delay regions only after t_0 allowed the signal to be refined to only include the $(p+, 0)_A$ channel, as the delayed onset of the $(p+, 0)_B$ channel results in this signal not appearing till later delays, and so averaging this short-delay signal gives the second basis function. The final basis function was obtained by averaging the late delay signal, which includes both dissociation channels, and then subtracting off the $(p+, 0)_A$ signal. This produced three basis functions where each only possesses a contribution from a single reaction channel, and these basis functions are shown for $I^{2/3/4+}$ in Figure 5.10. I^{6+} was excluded as the lower statistics made it impossible to extract accurate basis functions. The intensity of each basis function is set to zero at a manually chosen upper limit to prevent any noise in the low-intensity region from interfering in the quality of the fit, and additionally to help minimise any influence from the Coulomb curve merging with the channel. Additional intensity arising from the Coulomb curve fully merging with the channel at late delays was accounted for by scaling the intensity of the $(p+, 0)_B$ signal by $\sim 13\%$, determined by calculating the average increase in integrated intensity between 2-2.5 ps and 3.5-4 ps of a slice of the low momentum channel, to compare signal before and after the Coulomb curve has merged.

Each of these basis functions was used in a logistics function as shown in Equation 5.1:

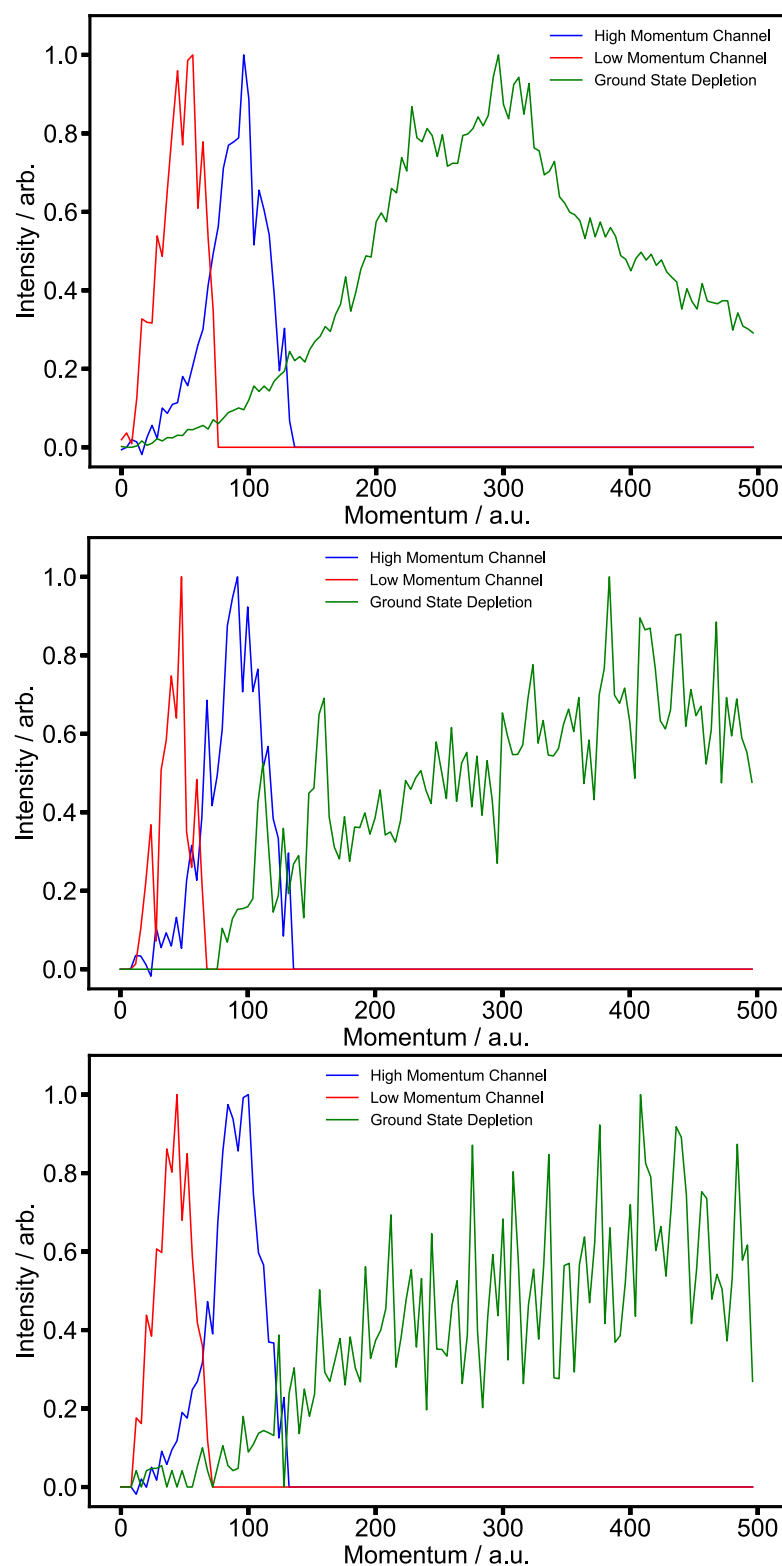


Figure 5.10: Extracted basis functions from the $I^{2/3/4+}$ momentum distributions for the ground state depletion and two dissociation channels, each scaled to their own maximum intensity.

$$\frac{A \times B_p}{1 + e^{-k(t-t_{\text{crit}})}}, \quad (5.1)$$

where A is the amplitude of the basis function, B_p is the momentum-dependent basis function itself, k is a rate constant, t is a delay value, and t_{crit} is the centre of the rise of the intensity in each logistics function (and therefore corresponds to the onset time of each channel), respectively. The experimental momentum distributions were fit to a sum of these three logistics functions (Equation 5.2) and optimised via least-squares fitting, which gives calculated signal intensity for each momentum, p , and delay, t , value:

$$I(p, t) = \frac{A_g \times B_g}{1 + e^{-k_g(t-t_{\text{crit}_g})}} + \frac{A_h \times B_h}{1 + e^{-k_h(t-t_{\text{crit}_h})}} + \frac{A_l \times B_l}{1 + e^{-k_l(t-t_{\text{crit}_l})}}, \quad (5.2)$$

where g , h and l correspond to the ground state depletion, high-momentum dissociation and low-momentum dissociation, respectively and $I(p, t)$ is the time- and momentum-dependent intensity. Plotting the momentum distribution of each iodine charge state after optimising these parameters gives $(p+, 0)$ channels that agree strongly with the experimentally observed signal. Subtracting the fit signal from the experimental data to give the residual signal also highlights the enhancement from the Coulomb curve, which is harder to distinguish in the experimental data due to its overlap with the $(p+, 0)_A$ signal. These experimental, fit and residual momentum distributions are given in Figure 5.11 for I^{2+} , and Figure 5.12 for $\text{I}^{3/4+}$, respectively.

Each optimised basis function, for each channel, in each iodine charge state, is shown in Figure 5.13, along with the optimised parameters of the logistics function. These optimised parameters, along with the basis functions themselves, can be used to interpret the dynamics of the two dissociations. Despite the ground-state having a very small amplitude, its inclusion is still required due to the signal at low momenta overlapping with the $(p+, 0)_A$ channel.

As the momentum of each iodine in the $(p+, 0)$ channels is purely dependent on the remaining energy after dissociation, the momentum of each iodine should be the same, irrespective of charge state. Plotting the extracted basis functions used in the global fit for each iodine charge state gives the 2D final momentum

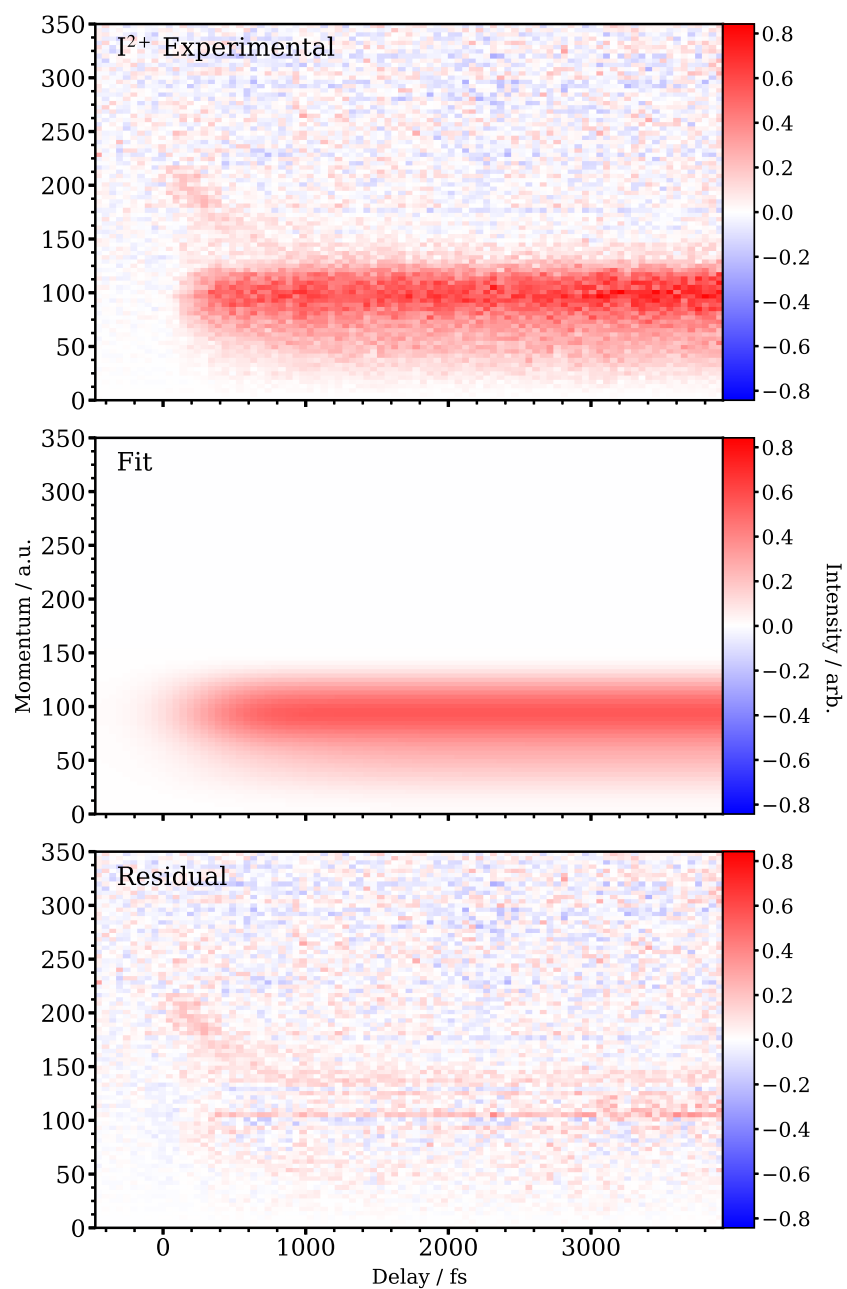


Figure 5.11: Experimental, optimised fit and residual momentum distributions for the I_2^+ data.

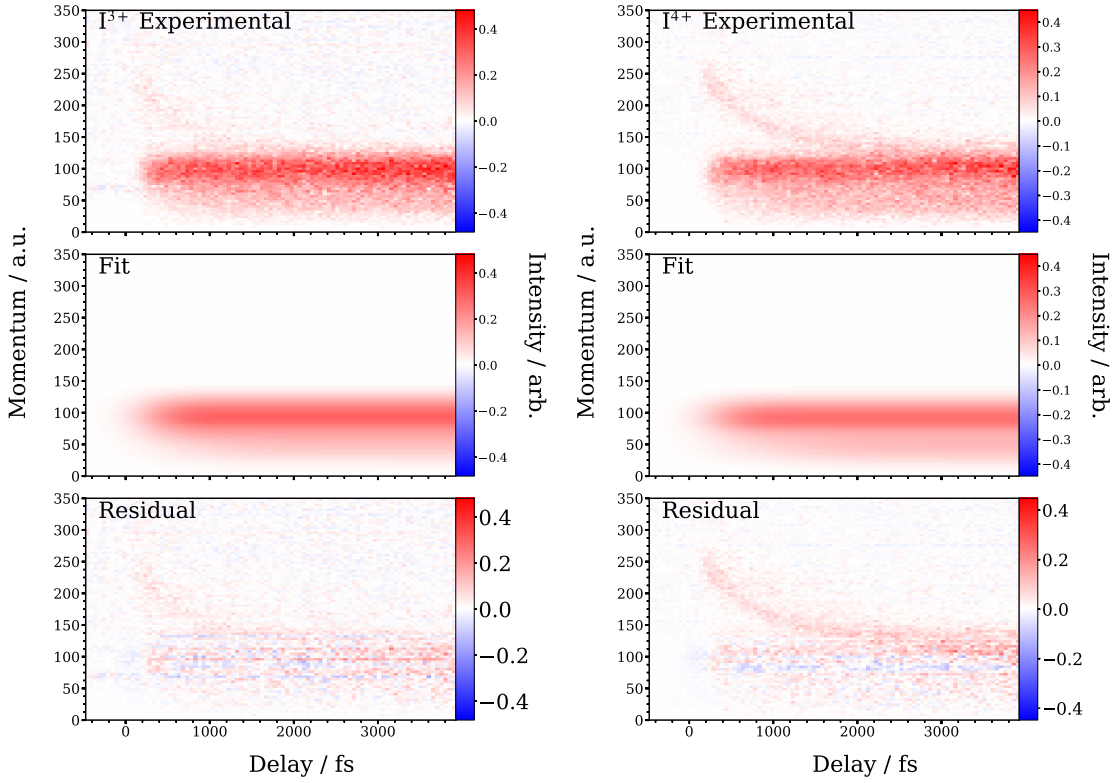


Figure 5.12: Experimental, optimised fit and residual momentum distributions for the $I^{3/4+}$ data.

distributions of each channel. These 2D momentum distributions are shown in Figure 5.14 and two sharp peaks were observed, again consistent with the two channels predicted by Hu *et al.*

Averaging the momenta across the different charge states (observed in Figure 5.14) gives a $(p+, 0)_A$ velocity of $870 \text{ ms} \pm 190 \text{ ms}^{-1}$, and a $(p+, 0)_B$ velocity of $420 \pm 130 \text{ ms}^{-1}$. Converting these velocities to total translational kinetic energy of the iodine and cofragment gives 1.32 ± 0.29 and $0.31 \pm 0.1 \text{ eV}$ for the two channels, respectively.

Using the extracted channel energies, Equation 5.3 was used to determine the amount of energy partitioned into the phenyl ring:

$$E_{\text{int}} = h\nu - T - D_{0,i} - E_e, \quad (5.3)$$

where $D_{0,i}$ corresponds to the dissociation energy of the channel, depending on the spin-orbit state of the iodine ion. For the $(p+, 0)_A$ channel this corresponds

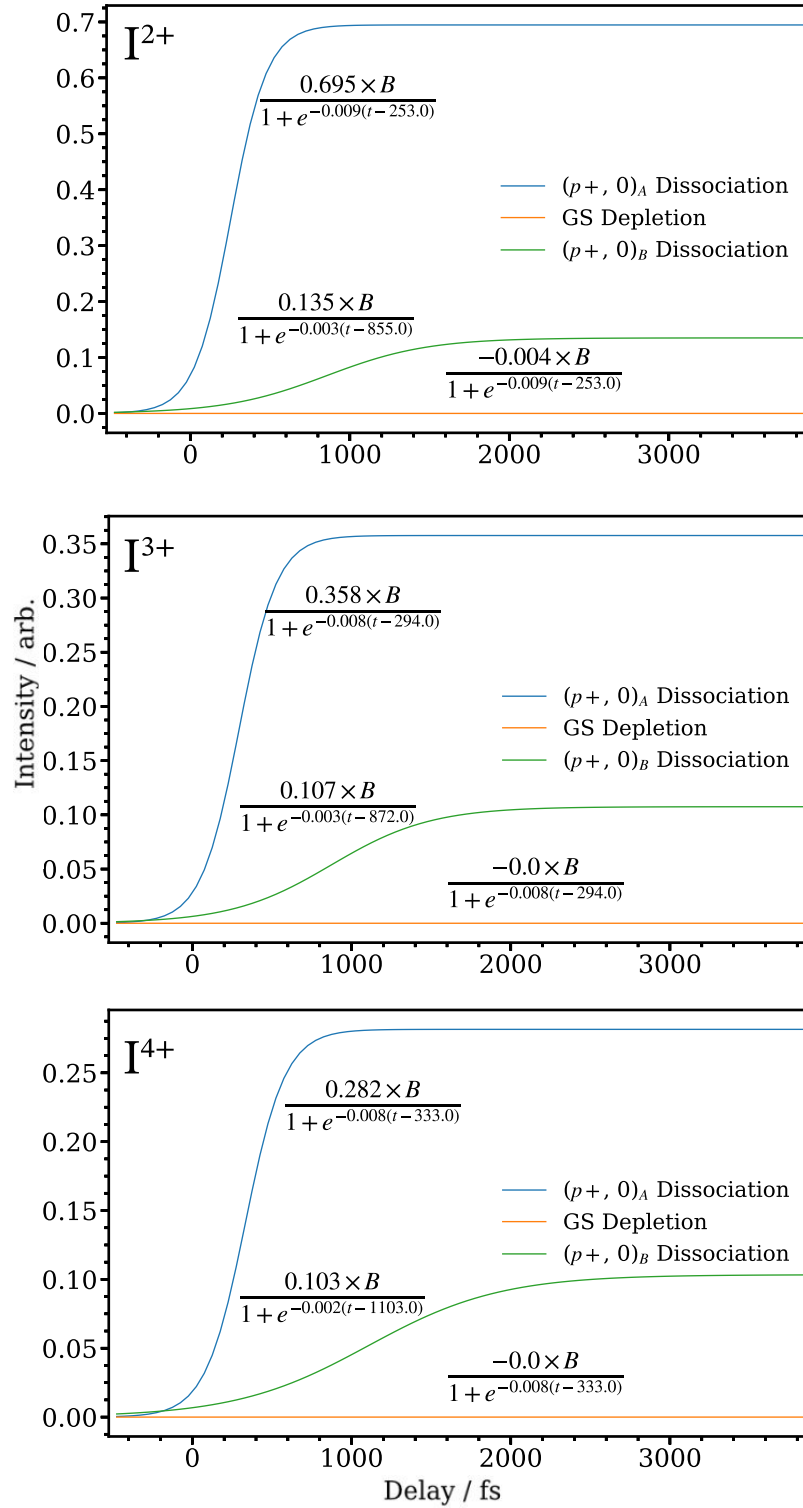


Figure 5.13: Plots of the optimised basis functions for the ground state depletion and two dissociation channels of $I^{2/3/4+}$ against time. The depletion curve has a very low amplitude, due to its very broad appearance (and low contribution to the low-momentum channels) (Figure 5.10).

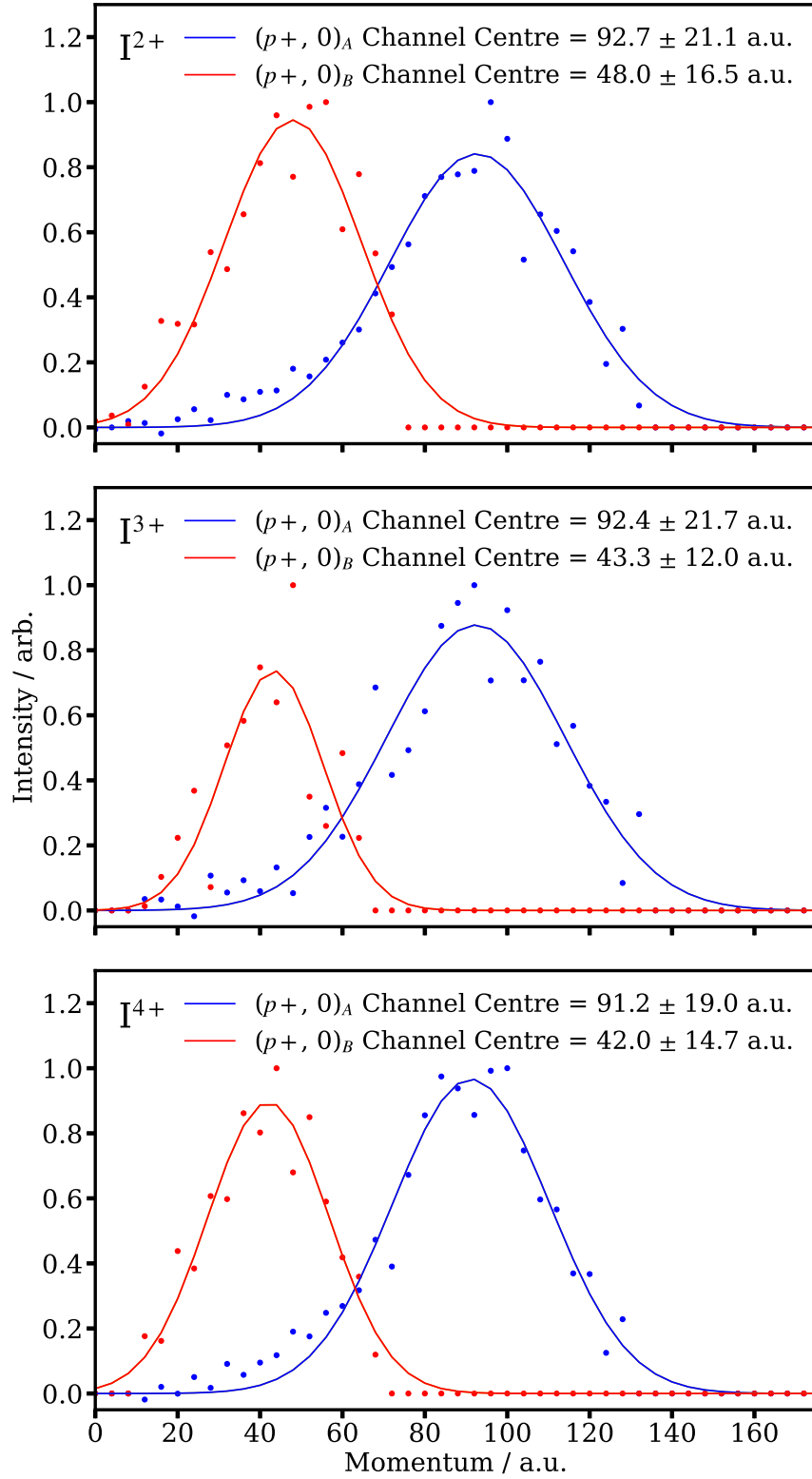


Figure 5.14: Momentum distributions obtained for the $(p+, 0)$ channels seen in the momentum distributions of $I^{2/3/4+}$. Obtained from the basis functions derived during the global fitting procedure. Each normalised to its own maximum intensity. Uncertainty corresponds to the σ value obtained from the Gaussian fit.

Table 5.1: Percentage of energy partitioned into internal energy of the phenyl ring during the photodissociation of iodobenzene. All energies reported in eV.

Channel	$I^{p+} E$	T	$D_{0,i}$	E_{int}	$E_{\%}$ (%)
Ph(X)	0.50 ± 0.11	1.32 ± 0.29	3.85	1.03 ± 0.23	44 ± 10
Ph(A)	0.12 ± 0.04	0.31 ± 0.10	2.9	0.57 ± 0.18	65 ± 21

Table 5.2: Branching ratio determined from the $(p+, 0)_A$ and $(p+, 0)_B$ dissociation channels using the basis functions and optimised amplitudes from the global fit. Averages are a weighted average based on the relative intensities of the I^{p+} channels.

Ion	$(p+, 0)_A$ (%)	$(p+, 0)_B$ (%)
I^{2+}	87 ± 2	13 ± 2
I^{3+}	89 ± 6	11 ± 6
I^{4+}	83 ± 15	17 ± 15
Average	87 ± 4	13 ± 4

to 3.85 eV, whilst for the $(p+, 0)_B$ channel this corresponds to 2.9 eV[97]. $h\nu$ is the energy of a 200 nm photon (6.2 eV), T is the translational kinetic energy of the two fragments, determined by assuming conservation of momentum and using the energy of the $(p+, 0)$ channels from the global fit. Finally E_e is the electronic energy of the Ph cofragment, corresponding to 0 eV for the $(p+, 0)_A$ channel, where a ground-state Ph(X) radical is produced, and 2.43 eV for the $(p+, 0)_B$ channel, where an excited-state Ph(A) radical is produced[110]. The results of this calculation are given in Table 5.1.

From Table 5.1, for the $(p+, 0)_A$ channel $44 \pm 10\%$ of available energy (2.35 eV) was partitioned into internal modes of the phenyl ring. For the lower momentum $(p+, 0)_B$ channel, this value was $65 \pm 21\%$ of available energy (0.87 eV).

The areas of the basis functions shown in Figure 5.14, along with the optimised amplitudes from the global fit, were used to characterise the branching ratio of the two channels. This is shown in Table 5.2. Here it was found that the $(p+, 0)_{A/B}$ channels, which as a reminder correspond to production of the $\text{Ph(X)} + I^*$ and $\text{Ph(A)} + I$ photoproducts respectively, have a branching ratio of 87:13 with an error of 4%. This value is similar to the branching ratio measured by Zhang *et al.* of 84:16 at 266 nm, despite exciting a different absorption band here.

Table 5.3: Optimised values of t_{crit} and k determined for each iodine charge state via the global fitting method. $t_{\text{crit}A}$ and k_A correspond to the optimised values for the $(p+, 0)_A$ channel, while $t_{\text{crit}B}$ and k_B correspond to the optimised values for the $(p+, 0)_B$ channel.

Ion	$t_{\text{crit}A}$ (fs)	$t_{\text{crit}B}$ (fs)	$k_A \times 10^{-3}$ (fs $^{-1}$)	$k_B \times 10^{-3}$ (fs $^{-1}$)
I $^{2+}$	253 ± 7	850 ± 70	8.8 ± 0.5	3.2 ± 0.6
I $^{3+}$	294 ± 6	870 ± 50	8.4 ± 0.4	3.2 ± 0.5
I $^{4+}$	333 ± 7	1100 ± 50	8.0 ± 0.4	2.4 ± 0.3

Rate constants, k , and onset times, t_{crit} , of the $(p+, 0)_A$ and $(p+, 0)_B$ channels were obtained from the optimised basis functions in Figure 5.13, and are given in Table 5.3 for each iodine charge state. Across the iodine charge states, the average rate constants of the dissociation channels are $8.4 \pm 0.4 \times 10^{-3}$ fs $^{-1}$ for the $(p+, 0)_A$ channel and $3.0 \pm 0.5 \times 10^{-3}$ fs $^{-1}$ for the $(p+, 0)_B$ channel. These rate constants can be converted into rise times for each dissociation channel, $(1/k)$, which gives rise times of 120 ± 5.8 fs and 333 ± 56 fs for the $(p+, 0)_A$ and $(p+, 0)_B$ channels, respectively. The rise time of the $(p+, 0)_B$ channel agrees with the the phenyl rise time reported by Hu *et al.* of 290 ± 90 fs, although it should be noted that due to their high signal-to-noise ratio they were unable to isolate rise times for the individual channels, and so did not report an independent rise time for the $(p+, 0)_A$ channel.

Finally comparison of the t_{crit} values obtained via the global fitting method to those obtained via the OTB model allows the electronic excited state of the cofragment to be determined, something that has previously not been achieved via analysis of the charge transfer channel. This was accomplished by comparison to an OTB model. As was explained in Section 2.5, the low momenta channels are absent at short delays due to stabilisation via a CT process, where at short delays an electron can migrate from a neutral fragment to stabilise a charged fragment, and those two charged fragments would Coulombically repel and not appear at low-momenta, giving a delayed onset to the channel. The OTB model provides a fragment separation, R_{crit} , at which CT no longer occurs, and this can be converted into a value for t_{crit} , using the known velocity of each channel. The comparison of these values to the values obtained via the global fit is shown for both channels in Table 5.4. Additionally, for the $(p+, 0)_A$ channel, comparison

Table 5.4: Experimental and calculated over-the-barrier model values for t_{crit} , the time at which charge transfer can no longer occur for each iodine charge state. Experimental values were calculated using the onset times of the observed charge transfer channels (obtained via both a cumulative distribution function, CDF, and global fitting (GF)). Over-the-barrier (OTB) time values were calculated using the R_{crit} value determined via the OTB model, which were subsequently converted into t_{crit} values using the $(p+, 0)$ channel velocities. A 50 fs error was propagated into the experimental uncertainties, to account for the precision of the t_0 assignment. Values are provided for the $(p+, 0)_A$ and $(p+, 0)_B$ channels, with the cofragment assumed to be either Ph(X) or Ph(A). All values reported in fs.

I^{p+}	$(p+, 0)_A$							
	CDF	Exp. t_{crit}	GF	Exp. t_{crit}	OTB t_{crit}	Ph(X)	OTB t_{crit}	Ph(A)
I^{2+}		240 ± 50		250 ± 50		290 ± 60		410 ± 90
I^{3+}		280 ± 50		290 ± 50		340 ± 70		470 ± 110
I^{4+}		320 ± 50		330 ± 50		380 ± 80		530 ± 120
I^{p+}	$(p+, 0)_B$							
			GF	Exp. t_{crit}	OTB t_{crit}	Ph(X)	OTB t_{crit}	Ph(A)
I^{2+}				850 ± 90		600 ± 190		850 ± 270
I^{3+}				870 ± 70		700 ± 220		990 ± 310
I^{4+}				1100 ± 70		780 ± 250		1100 ± 350

is also made to t_{crit} values obtained via fitting a CDF to the channel (shown in Figure 5.15), and the strong agreement between the CDF and global fit values provides further evidence as to the effectiveness of the global fit in characterising these channels. Due to the overlap of the $(p+, 0)_B$ channel with the $(p+, 0)_A$ channel, a CDF value was unable to be obtained for this channel, demonstrating the global fit model is a more viable method to extract these time values when multiple overlapping channels are detected.

To account for the different excited states of the phenyl ring, different ionisation potentials were used and OTB values for both cofragments are included in Table 5.4. For the Ph(X) fragment, an ionisation potential of 8.32 eV was used. For the Ph(A) fragment, the ionisation potential was changed to 5.89 eV, to account for the higher energy of a Ph(A) fragment[110, 111]. A strong agreement can be seen between the experimental and OTB values for t_{crit} when assuming a Ph(X) cofragment in the high-momentum channel, and when assuming a Ph(A) cofragment in the low-momentum channel, confirming the $(p+, 0)_A$ channel produces a ground-state

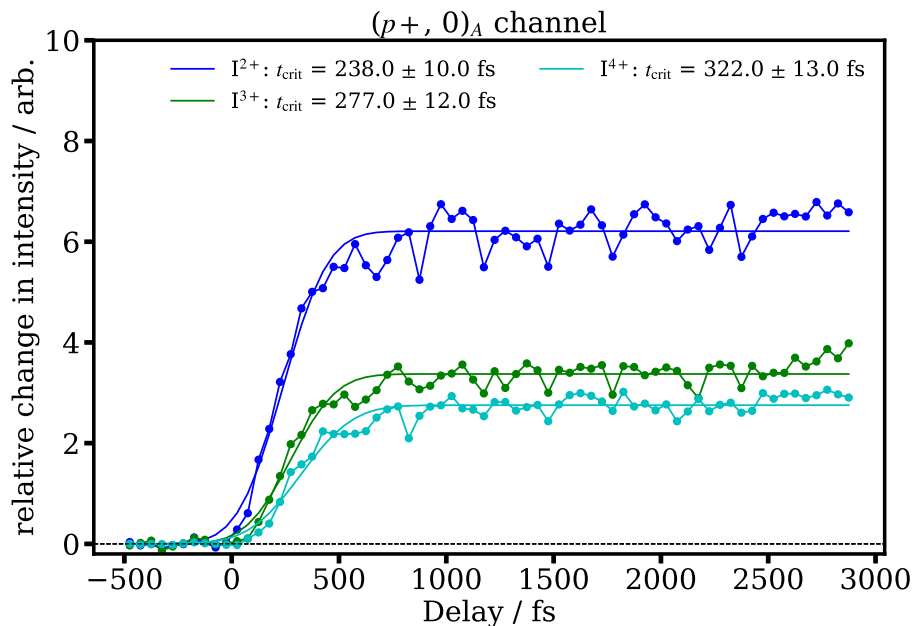


Figure 5.15: CDF fit to the $(p+, 0)_A$ channel of $I^{2/3/4+}$.

Ph(X) fragment, while the $(p+, 0)_B$ channel produces an excited Ph(A) product. This result demonstrates the capability of the charge transfer channel to identify the electronic state of the cofragment, which, as mentioned earlier has not been previously accomplished using charge transfer data, and further increases CEI's suitability to characterise photochemical reactions.

$(p+, 1+)$ Channel

The lack of further energy for dissociation of the phenyl ring[112], and the strong agreement between the OTB and experimental onset times indicates that a phenyl radical is the cofragment to the dissociation. Given that, Coulomb curves were expected in the phenyl momentum distribution (shown in Figure 5.16) or in other carbon fragments, as curves were observed in the iodine momentum distributions, and such curves require the existence of one or more charged species to recoil against. The lack of time-dependence in the carbon fragments means that it was not possible to directly confirm the dissociation cofragment in this experiment. Instead, the earlier evidence was supported by producing modelled Coulomb curves for each iodine recoiling against different possible cofragments.

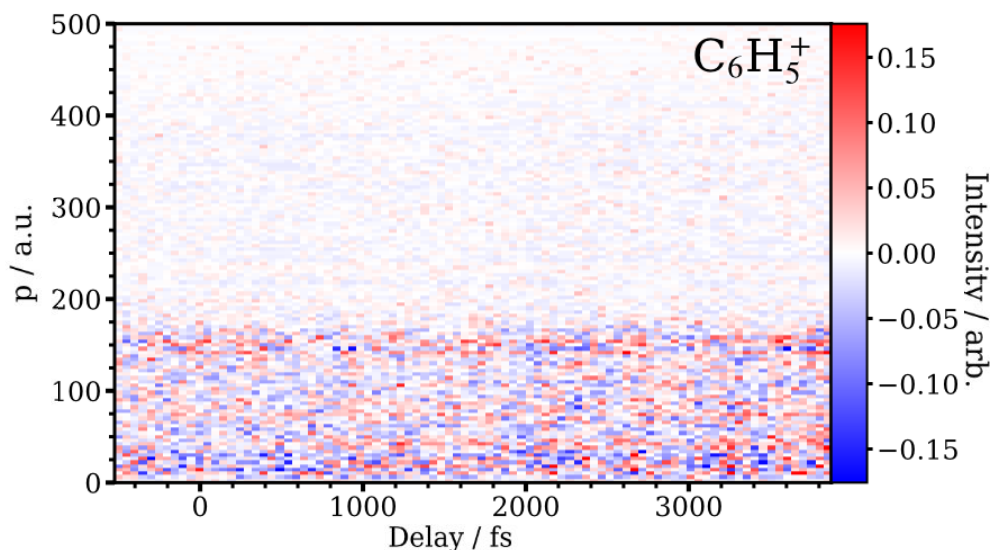


Figure 5.16: Background-subtracted momentum distribution of the phenyl ion signal. Subtraction was accomplished in the same manner as the iodine distributions shown in Figure 5.9, by removing an average of the data pre- t_0 .

Taking the neutral dissociation velocities from the global fit (which should be equivalent to the Coulomb curve asymptotic velocities at long delay times where the Coulombic component is negligible), and using Coulomb's Law to determine the Coulombic component at different fragment separations, simulated Coulomb curves were produced at each delay value. These modelled curves (assuming recoil against a $C_6H_5^+$ fragment) are superimposed on the experimental curves in Figure 5.17, and strong agreement between the experimental and modelled curves was seen for each iodine charge state.

For the distributions in Figure 5.17 the charge on the phenyl radical was placed on the site of C-I cleavage. It is shown in Figure 5.18 that shifting the charge away from the site of C-I cleavage does not significantly change the agreement with the experimental measurements, with far more significant changes observed when changing the size of the cofragment or the charge of the cofragment (as will be demonstrated below). Shifting the location of the charge was accomplished by adjusting the initial distance used for the separation of the two charges when producing the curves. These distances were 2.079, 3.025, 4.340, 4.865 and 3.472 Å, corresponding to placing the charge on the carbon at the site of C-I cleavage, the

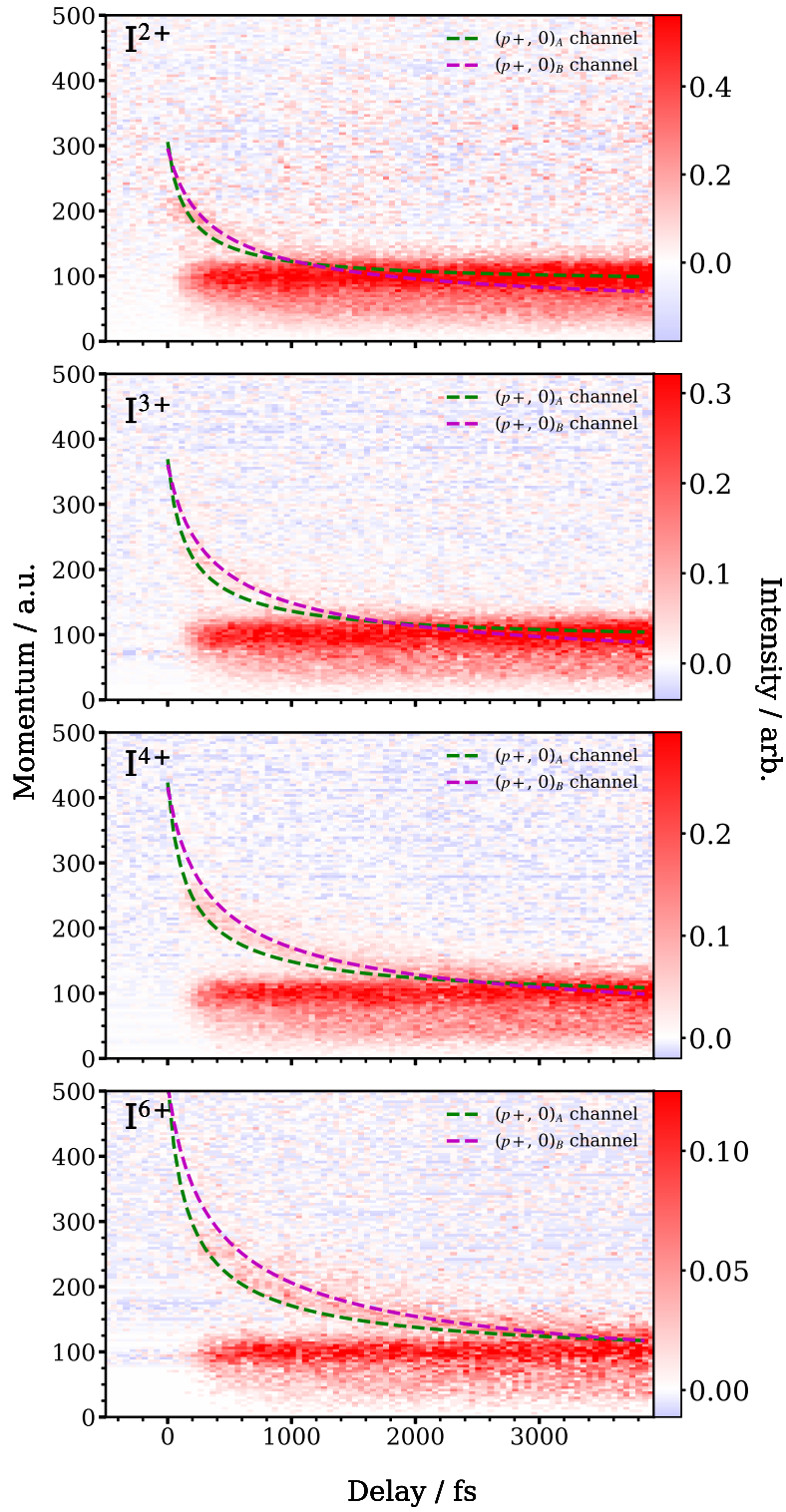


Figure 5.17: Simulated Coulomb curves compared to background-subtracted experimental data for $I^{2/3/4/6+}$. Charge is assumed to be located on the site of C-I cleavage.

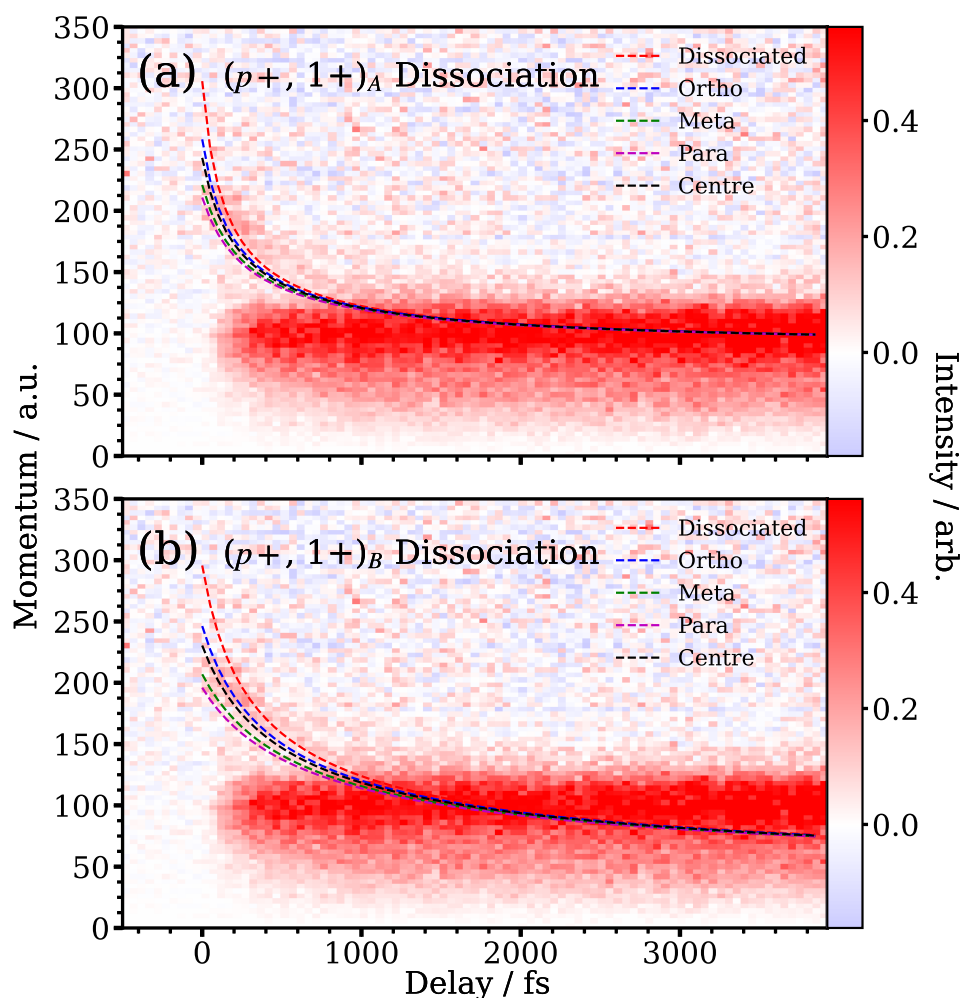


Figure 5.18: Effect of changing the location of the charge on the phenyl ring on the simulated Coulomb curves for the $(p+, 0)_A$ (panel (a)) and $(p+, 0)_B$ (panel (b)) dissociations of I^{2+} .

ortho-, meta- or para- carbons, and the centre of the phenyl ring. The separations were determined using the Avogadro software package[113].

A worse agreement was found when using different fragments to a $C_6H_5^+$ ion as the cofragment to the dissociation, and examples of this are shown in Figure 5.19, which shows the effect of modelling the curves using (a) a $C_3H_3^+$ fragment (formed by the phenyl radical splitting into two equal mass fragments) and (b) using a doubly charged phenyl radical. In both cases the agreement between the experimental and modelled curves is considerably less, supporting the assignment of a singly charged phenyl radical being the cofragment.

The lack of energy for further dissociation, the strong OTB agreement, and

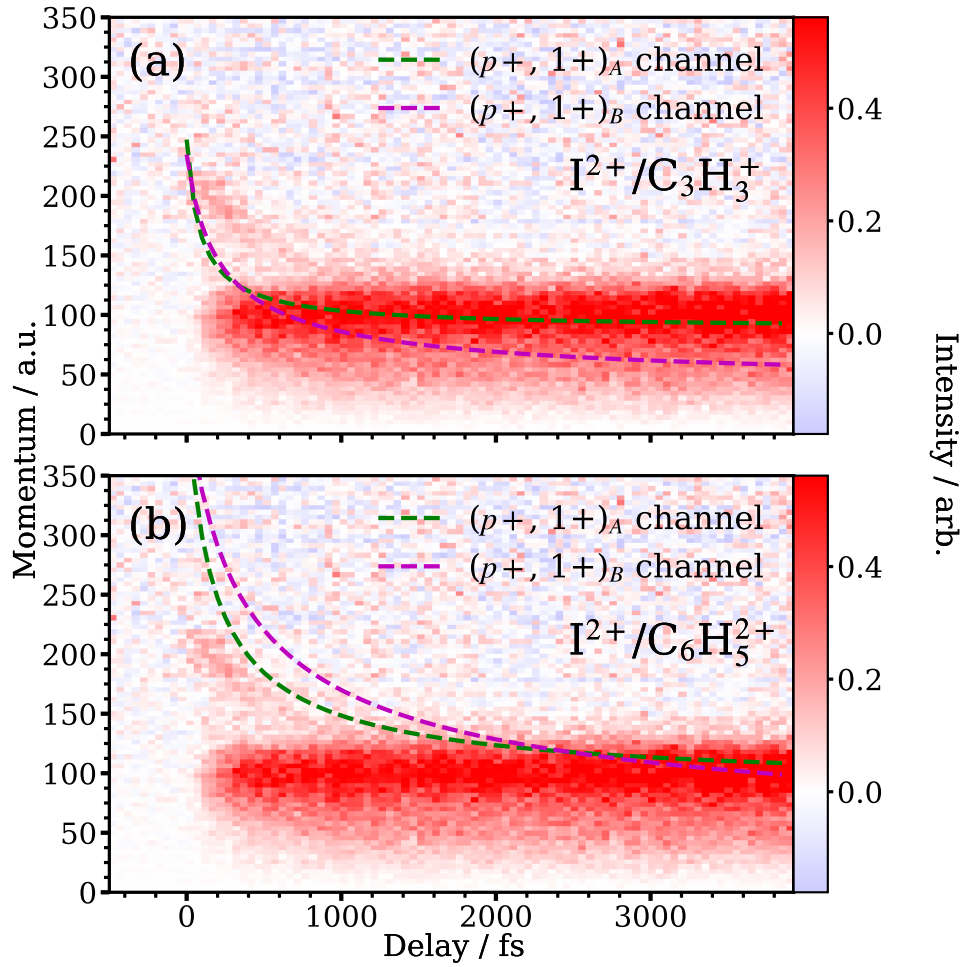


Figure 5.19: Effect of changing the model so that the I^{2+} ion recoils against (a) a C_3H_3^+ ion and (b) a $\text{C}_6\text{H}_5^{2+}$ ion.

the strong agreement of the modelled curves all indicate the cofragment to the dissociation is a phenyl radical. The lack of time-dependence in the phenyl momentum distribution is, as mentioned above, therefore surprising, as the strong Coulomb curves in the iodine distributions require a charged cofragment. This lack of time-dependence was therefore attributed to the instability of the phenyl radical after XUV ionisation, leading to the occurrence of multiple fragmentations after ionisation with the intense XUV pulse, that occur prior to interaction with the detector[114].

5.4 Results and Discussion - UV/IR

Given that the above cofragment assignment is based on indirect measurements, additional data was collected using a UV/IR experimental setup, where it was

hoped that the different ionisation regime would leave the phenyl radical intact after ionisation. The majority of this analysis will use the ‘zoomed in’ voltages described in the experimental section, as with the available IR intensity, the majority of Coulombically repelling iodine fragments were singly charged. Data were recorded from -1 ps to 3.5 ps to provide a similar delay range to that used in the UV/XUV study.

Figure 5.20 shows the mass spectrum for the collected UV/IR data across all delay ranges. Labelled are I^{1-2+} and the possible phenyl fragments from C₆H₅. Note there is no CH⁺ fragment due to the gating unit removing any ions with a mass below water. Unlabelled peaks correspond to remaining contaminants in the chamber from previous experiments.

For each of the ions seen in the mass spectrum, delay-dependent momentum distributions were produced. These are shown in Figure 5.21, with 100 fs delay bins, and a strong time-independent signal is seen in all ions. Similar to the XUV-only data, when the IR pulse interacts with a ground-state iodobenzene molecule the parent can fragment into multiple different combinations of ions. It should be cautioned that due to the more limited resolution of the experimental setup, and contamination in the chamber, there is overlap between the lower mass ToF peaks, resulting in far greater noise compared to the I⁺ and Ph⁺ fragments.

Similar to the XUV data, time-dependence was enhanced by removing an average of the signal pre- t_0 , and therefore before any contributions from the UV pulse. As was suggested by the UV/XUV analysis, no time-dependence was seen in any of the smaller carbon fragments that would have been produced by a phenyl radical undergoing a secondary dissociation. However, unlike the UV/XUV data, a Coulomb curve was visible in the C₆H_{*n*}⁺ ion signal. Shown in Figure 5.22 are unsubtracted and background-subtracted momentum distributions for I⁺ and C₆H_{*n*}⁺ for 100 fs delay bins around t_0 (panels (a)-(d)), while panels (e) and (f) show coarse background-subtracted scans with 200 fs bins to later delays. The existence of time-dependence in the phenyl radical, as well as in I⁺ supports the earlier assumption that in the UV/XUV experiment the lack of time-dependence in any

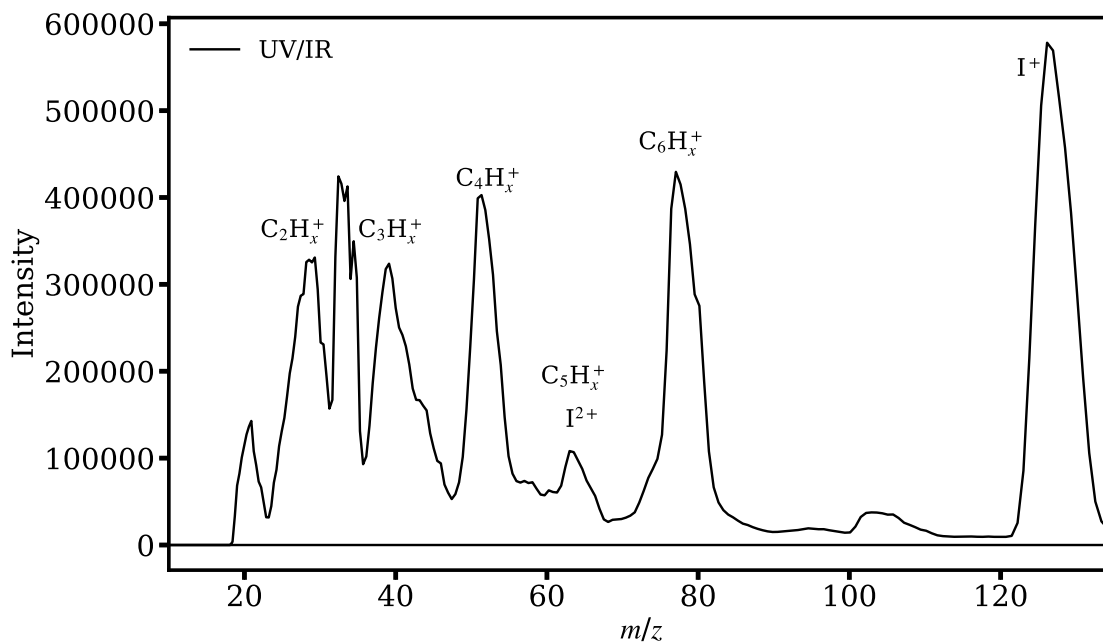


Figure 5.20: Mass spectrum for the UV/IR data. Seen are I^{1-2+} and $C_yH_x^+$ where $y = 1-6$ and $x = 1-5$.

carbon containing fragments is the result of phenyl fragmentation prior to interaction with the detector. The lack of any time-dependence in the smaller carbon fragments also supports the statement that no further dissociation of the phenyl radical occurs, and hence charge transfer occurs from $C_6H_n^+$, as predicted via the UV/XUV OTB comparison. To check that the Coulomb curves had reached their asymptotic values (given that there is no charge transfer channel to compare to), a coarse delay scan using 200 fs bins out to late delays was performed (data was collected from -1 to -0.4 ps for background subtraction, and then from 3.5 to 7.5 fs). These scans can be seen in Figure 5.22(e) and (f) for I^+ and $C_6H_n^+$, respectively, and it can be seen that no further change in the channel occurs at late delays, showing that Coulombic repulsion is negligible at 3.5 ps.

Recoil-frame covariance analysis (Section 3.4.5) (shown in Figure 5.23) confirmed that the time-dependent Coulomb curves in I^+ and $C_6H_n^+$ were produced in the same two-body reaction channel. Time-dependent covariance was performed by collecting high statistic data at three discrete delay points: -1 ps to give background data, corresponding to probing of the ground-state molecule, 0.4 ps (UV just early)

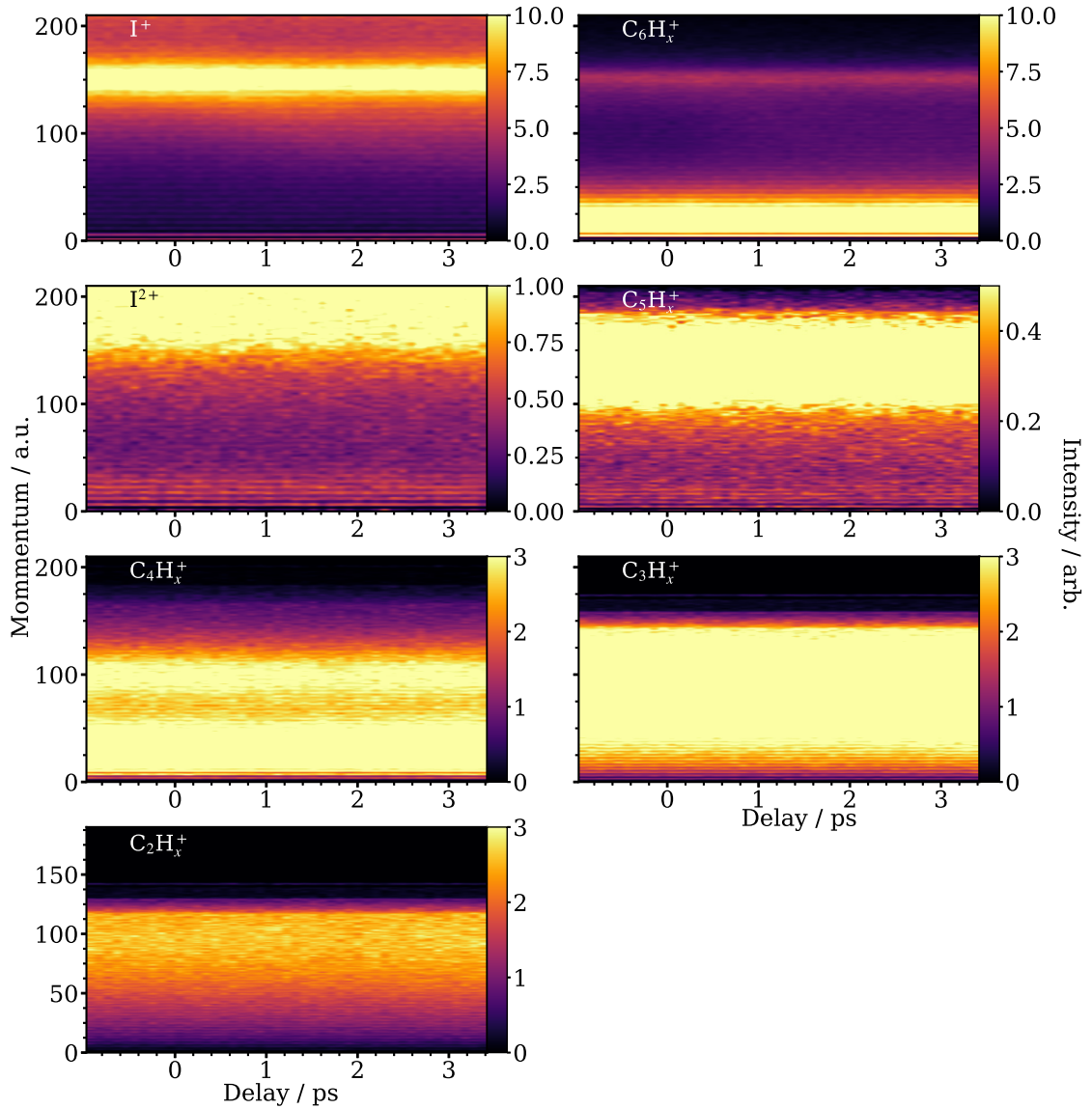


Figure 5.21: Unabstracted momentum distributions for the UV/IR data for I^{1-2+} and $C_yH_x^+$ where $y = 1-6$ and $x = 1-5$.

to represent a short delay region where there is high Coulombic repulsion (i.e. within the Coulomb curve), and 3.5 ps (UV very early) to account for the region in which Coulombic repulsion is negligible.

It can be seen in Figure 5.23 that in all panels a positive covariance signal is seen at 180° , consistent with a two-body recoil. The existence of the signal after removal of the UV-late contribution confirms that the I^+ and $C_6H_n^+$ Coulomb curves are produced from the same reaction channel. This is further supported by the larger radii seen in the UV just early (corresponding to the UV arriving 0.4 ps prior

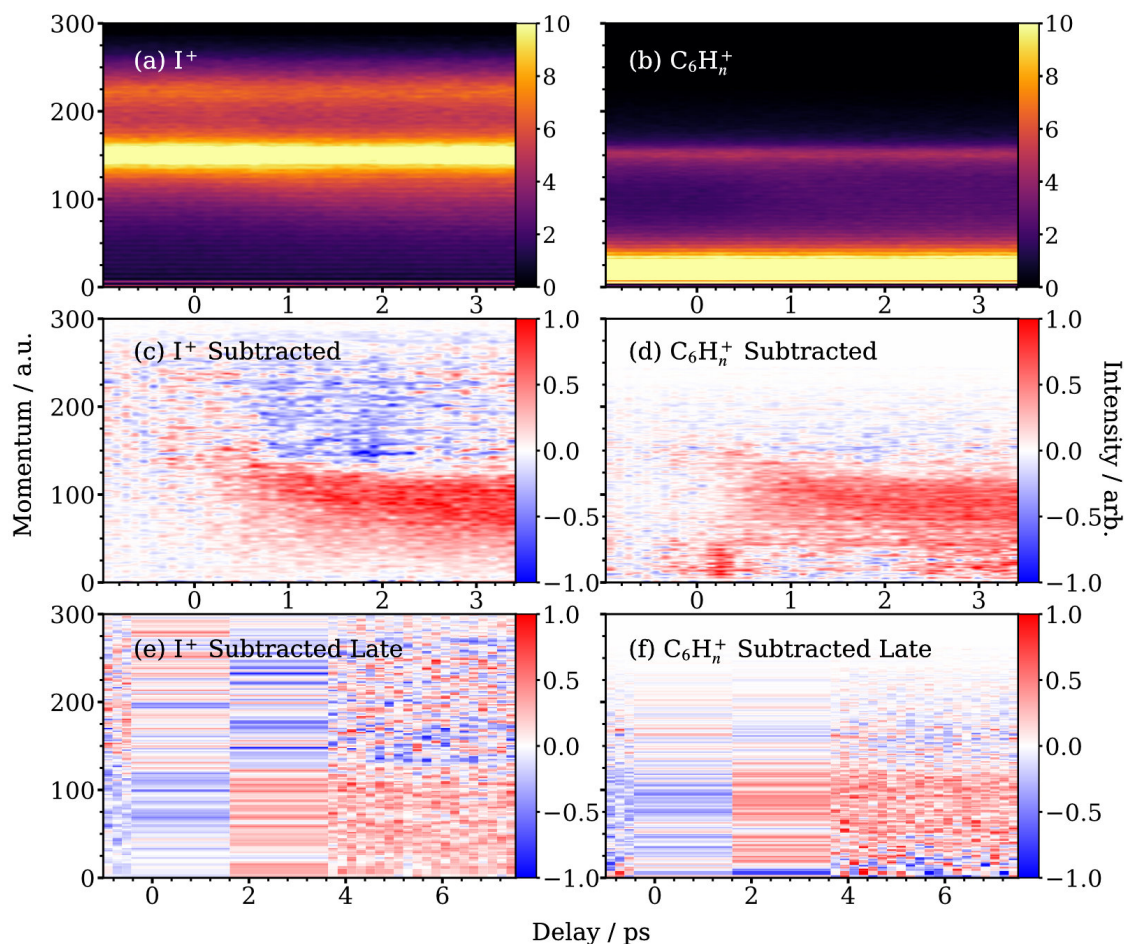


Figure 5.22: Unsubtracted and background-subtracted momentum distributions for the I^+ and C_6H_n^+ ion signals. Panels (a)-(d) show a fine scan around t_0 , while panels (e) and (f) show a coarse scan out to late delays.

to the IR) compared to UV very early (3.5 ps prior to the IR). This decrease in radii corresponds to a decrease in fragment momenta, and is as expected with a dissociating charged molecule, with later delays giving greater fragment separation and therefore less Coulombic repulsion between fragments.

The final figure in this Chapter is an I^{2+} subtracted momentum distribution, shown in Figure 5.24. This distribution was produced after acquiring a delay scan at the zoomed out VMI voltages described in the experimental section. This momentum distribution shows that similar chemical dynamics occur in the higher charge state iodines as they do in I^+ , and therefore further supports the explanation for the lack of UV/XUV time-dependent phenyl signal. The lower resolution of the I^{2+} Coulomb curve is a consequence of the experimental setup here producing a

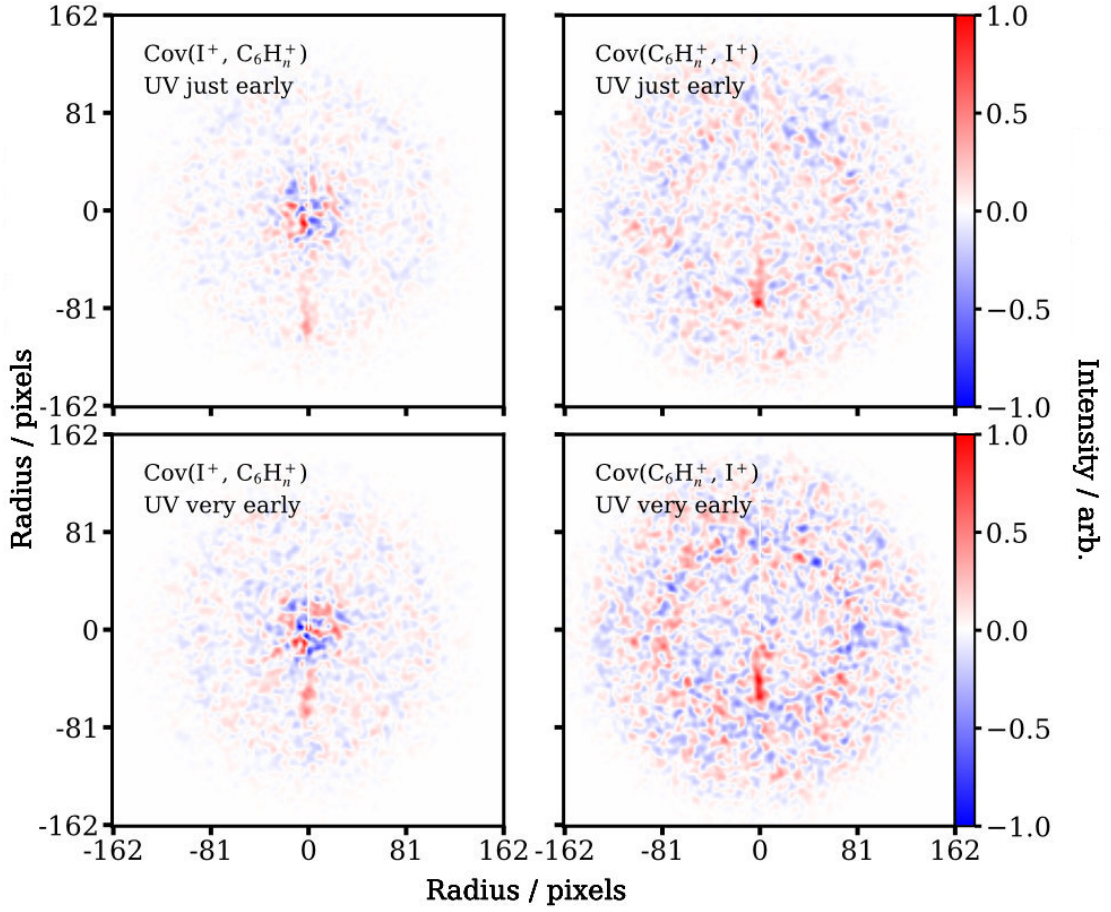


Figure 5.23: Covariance images for UV just early and UV very early delay regions for I^+ recoiling against $C_6H_n^+$ and $C_6H_n^+$ recoiling against I^+ . UV just early corresponds to the UV pulse arriving 0.4 ps prior to the IR pulse, while UV very early corresponds to the UV pulse arriving 3.5 ps prior to the IR pulse.

much lower count of I^{2+} ions. Acquiring for a significantly longer period of time to increase statistics would potentially improve the quality of this curve, but its existence is sufficient to the desired purpose in this experiment.

5.5 Summary

In this Chapter, CEI, along with the dynamics from sole ionisation of the dissociated iodine, were used to characterise the properties of two competing dissociation channels, and additionally to identify the cofragment to the dissociation. Using a 200 nm UV/10.3 nm XUV pump-probe regime in iodobenzene, two overlapping ($p+$, 0) channels were seen, corresponding to a high momentum channel giving

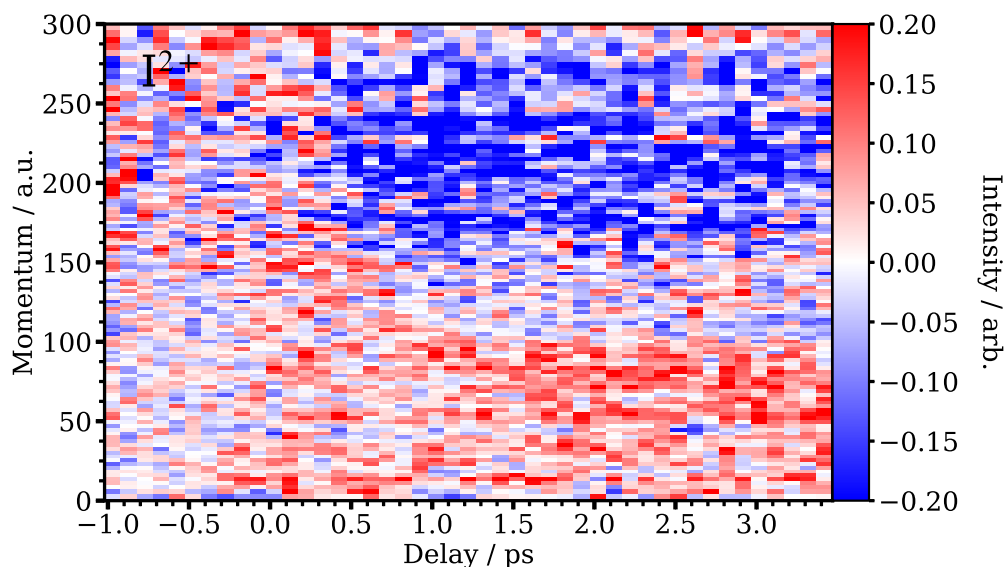


Figure 5.24: I_2^+ subtracted momentum distribution recorded at ‘zoomed out’ VMI voltages designed to better detect high velocity fragments.

$\text{Ph(X)} + \text{I}^*$ photoproducts, and lower momentum channel corresponding to $\text{Ph(A)} + \text{I}$ photoproducts. The existence of two dissociation channels was consistent with a previous study by Hu *et al.*, which found at 200 nm initial excitation occurred to the $7\text{B}_1/7\text{B}_2$ states, followed by rapid relaxation to the 7A_1 and 8B_2 states. From here the molecule can either remain on the $7\text{A}_1/8\text{B}_2$ states and subsequently dissociate to give the $\text{Ph(A)} + \text{I}$ products ($(p+, 0)_B$ channel), or it can transition to the lower energy 7B_2 , 8A_2 and 8B_1 states, where dissociation occurs to give $\text{Ph(X)} + \text{I}^*$ ($(p+, 0)_A$ channel). The dynamics of these channels were explored using a global fitting method that utilises three basis functions corresponding to the three processes occurring in this momentum range.

The amount of energy partitioned into the phenyl ring for each channel was calculated using the total translational kinetic energy obtained from the global fit, and, for the $(p+, 0)_A$ and $(p+, 0)_B$ channels, respectively, $44 \pm 10\%$ and $65 \pm 21\%$ of available energy was partitioned into the phenyl ring. Branching ratios of the two channels were found by analysis of optimised global fit amplitudes and basis functions, and gave a ratio of 87:13 for the $(p+, 0)_A:(p+, 0)_B$ dissociations, respectively, with an error of 4%. This value is similar to that obtained at 266 nm by Zhang *et al.* of 84:16, despite significantly different reaction channels[101]. Rate

constants and rise times of the two channels were measured as $0.0084 \pm 0.0004 \text{ fs}^{-1}$ and $120 \pm 5.8 \text{ fs}$ for the $(p+, 0)_A$ channel, and $0.0030 \pm 0.0005 \text{ fs}^{-1}$ and $333 \pm 56 \text{ fs}$ for the $(p+, 0)_B$ dissociation. Finally, the onset times of each channel determined by the fit were compared to those predicted via an over-the-barrier model, with different ionisation potentials being used to account for the different excited states of the Ph radical. For the $(p+, 0)_A$ channel strong agreement was found using the ionisation potential of a ground-state Ph(X) radical, while for the $(p+, 0)_B$ channel strong agreement was found using the ionisation potential of an excited-state Ph(A) radical. This decisively shows the capability of the charge transfer channel to deduce the excited state of a cofragment after a dissociation, and demonstrates that a similar approach could be applied in novel experiments where cofragments are produced in multiple excited states.

No time-dependence was observed in any of the carbon containing cofragments after interaction with the probe pulse, due to it fragmenting into multiple pieces prior to interaction with the detector. Due to the lack of remaining energy for further fragmentation of the phenyl ring, it was assumed that the cofragment to dissociation was a phenyl radical. This was supported by strong agreement between the experimental onset times of each channel and those predicted via an OTB model. This assignment was further supported by simple modelling of the time-dependent Coulomb curves ($(p+, 1+)$ channel) with various potential fragments, with strong agreement seen when utilising a phenyl radical as the cofragment.

The cofragment identification was then directly confirmed by additional experimental data collected using a 200 nm UV/800 nm IR regime, where the different ionisation regime accessed via an IR probe pulse enabled direct measurement of C_6H_n^+ , where a time-dependent Coulomb curve was observed. Recoil-frame covariance analysis was then used to ascertain that the C_6H_n^+ fragment was produced in the same two-body reaction channel as the time-dependent feature seen in I^+ .

This Chapter gives evidence for CEI's capability to distinguish and characterise the properties of two overlapping dissociation channels produced after excitation to high-lying excited states, including their branching ratios, internal energy

deposition, rise times, and cofragment excited states. Additionally, it shows how using these data values in simple models allows determination of the cofragment to the dissociation, without it being directly observed. Similar models can be applied in future photodissociation studies to identify the products in situations where one or more photoproducts are unstable after ionisation and therefore fragment prior to interaction with the detector.

6

Determining the Transient Excited-State Geometry of CS₂

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6.1 Background

Thus far, this thesis has demonstrated how CEI can be used to distinguish between two- and three-body photodissociation mechanisms, and to determine the properties of competing photodissociations. This Chapter instead focuses on CEI's sensitivity to the geometry changes a molecule can undergo prior to dissociation.

To that end, this Chapter uses time-resolved 3D momentum and covariance

imaging to extract information about the dissociation dynamics of carbon disulfide, by looking at the fragments produced after Coulomb explosion. As the FEL can access a large number of different charge states across the sulfur and carbon atoms, many reaction channels exist where the total charge on the molecule is the same, but this charge is distributed differently amongst the three atoms. This same total charge results in many reaction channels overlapping in their momentum, as the repulsion between a 1+ and 2+ ion will be broadly similar irrespective of which atom is singly- or doubly-charged (as the bond lengths are roughly similar) and hence the origin of each signal can be hard to elucidate. To separate out the combined signals into their individual components, the data here was supported via a simple Coulomb explosion model that is explained in more detail in Section 6.3.3.

The target molecule of CS₂ was selected due its previously well-studied photodynamics, enabling the CEI measurements to be benchmarked. Despite significant interest in CS₂, a full accounting of its photodynamics has historically been difficult to obtain via a NIR-probe pulse, predominantly due to field-induced coupling of electronic states, which leads to motion along the bending-coordinate and hence Coulomb explosions at longer bond-lengths than expected[115]. Ionisation with the soft X-ray pulse here causes relatively rapid core ionisation and avoids these issues, demonstrating the advantages of utilising an FEL to conduct this study.

The existing literature shows excited CS₂ exhibits many interesting ultrafast photochemical processes. CS₂ undergoes dissociation into both singlet and triplet sulfur atoms, and their correlated CS fragments, on a timescale of less than one picosecond. This dissociation is dominated by production of the spin-forbidden triplet state, with a triplet to singlet branching ratio of $\sim 2.5:1$ [116]. Work by Smith *et al.* and Suzuki *et al* has attributed this branching ratio to internal conversion leading to the fast formation of a metastable intermediate, which subsequently produces the triplet product via intersystem crossing[117, 118]. The dissociative decay of excited CS₂ has been reported to occur via two timescales. Firstly, a route taking ~ 50 -70 fs, and then a slower 500-800 fs route[119, 120].

However work by Fuji *et al.* failed to observe a rapid decay, only seeing evidence of a 400 fs dissociative lifetime[121].

While excited, but prior to dissociation, CS₂ undergoes a large degree of bending and stretching motion[119, 122, 123]. The mean bend angle of the excited molecule has a reported range of 115-153°[124, 125], with the C-S bond length stretching from 1.55 Å to 1.65 Å[125].

This wide variety of different excited state geometry changes and dynamics make CS₂ ideal to explore CEI’s sensitivity to such changes on femtosecond timescales. The following discussion will follow the ultrafast non-Born-Oppenheimer photodissociation dynamics (that is, dynamics that involve a change in the electronic states of the molecule, without any emission of radiation, and where the electronic and nuclear trajectories are not separated[126]). This was accomplished using a 201.5 nm UV pump and 6.9 nm XUV probe regime.

Figure 6.1 shows a schematic overview of the expected geometry changes after excitation, with CS₂ proceeding from a linear ground state to the excited $^1\Sigma_u^+$, where it undergoes bending and stretching motions followed by relaxation to the $^1\Delta_g$ state, followed by dissociation. Depending on which location on the potential energy surfaces the molecule is probed, the resultant signals will possess different momenta, allowing their nature to be disentangled (within the resolution of the experiment). The potential energy surfaces were simulated by Wang *et al.*, using a complete active space self-consistent field (CASSCF) method, using a (10,8) active space which then incorporated dynamic correlation at the multi-reference configuration interaction with single excitations (MR-CIS) level of theory and using an atomic natural orbital (ANO) basis: 3s2p1d for C and 4s3p2d for S[127]. Figure 6.1 is only intended to provide a brief overview of the expected transitions and motion of CS₂ throughout this experiment, and so only states relating to the singlet photoproducts are provided, but as mentioned above there is additionally a significant triplet contribution ($\sim 2.5:1$)[116]. The following analysis shows how CEI is sensitive to the aforementioned bending on a transient excited state, and how covariance analysis of the CEI data can extract a bend-angle of the excited molecule.

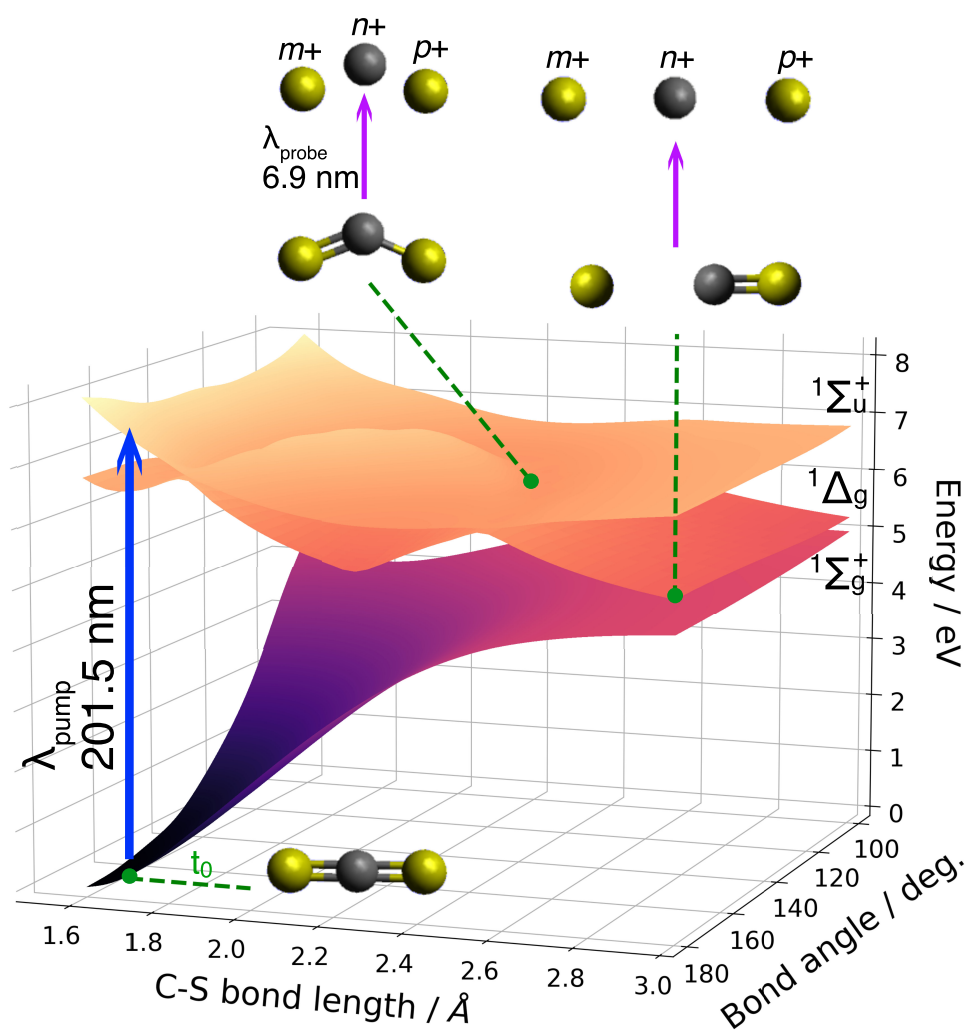


Figure 6.1: Simulated singlet potential energy surfaces for CS₂. The 201.5 nm UV pulse excited the linear ground state molecule to the $1\Sigma_u^+$ state. After excitation, the molecule undergoes bending and stretching motions before subsequently decaying to the $1\Delta_g$ state and dissociating. *m*, *n* and *p* correspond to the charge states that were observed after ionisation by the probe pulse, with *m* and *p* ranging from 0-4+, and *n* from 0-2+. Surfaces simulated by Wang *et al.*[127]. For simplicity, only a subset of the accessible excited states are shown.

6.2 Methods

6.2.1 Experimental Setup

The data in this Chapter was collected using the CAMP@FLASH end-station at beamline 1 (BL1) at FLASH[48, 128]. A 12 mJ, 55 fs, 800 nm IR pulse was used to generate the UV pump pulse. This was accomplished by first passing the IR pulse through a beamsplitter to separate out 50% of the beam. This fraction of the beam was passed through two β -BBO crystals, to frequency triple the beam, which was subsequently passed through dichroic mirrors to separate the third harmonic. The previously unused transmitted component of the original IR beam was split again with another 50:50 beamsplitter, and the obtained 25% fraction combined with the third harmonic to produce the fourth harmonic via sum-frequency mixing[129]. The produced 201.5 ± 0.4 nm UV pulse had an average energy of 0.45 ± 0.0009 μ J after generation. This resulted in a pulse energy of 0.22 ± 0.0004 μ J at the interaction region, due to a total reflectivity of 48% on the steering mirrors that guided the pulse into the chamber. Two colour (UV/IR) non-resonant multiphoton ionisation of Xe⁺/Xe²⁺ was used to determine the duration of the UV pulse. This measurement calculated a UV/IR cross-correlation of 150 fs (Figure 6.2). Using the known IR temporal duration of 55 fs, this gives a UV pulse duration of 140 fs. This UV duration can then be used with the measured focal spot diameter of 30 μ m, to obtain a UV intensity of $2.1 \pm 0.004 \times 10^{11}$ W cm⁻².

CS₂ was ionised by core-orbital ionisation using a ~ 6.9 nm soft X-ray probe pulse (~ 180 eV). This pulse energy was tuned to ionise just above the S 2p edge, and largely resulted in double ionisation of CS₂[130, 131]. The average FEL pulse energy was 54 ± 10 μ J, and the full FEL energy distribution used for the analysis here is shown in Figure 6.3. Considering the energy losses due to reflectivity and transmission of the mirrors along the beamline, the average FEL energy in the interaction region was 23 ± 4.3 μ J. Variations in FEL parameters throughout the experiment were measured using the Gas Monitor Detector, the bunch arrival monitor, and electron bunch charge, photon spectra and the transverse deflecting cavity ‘LOLA’[91, 132,

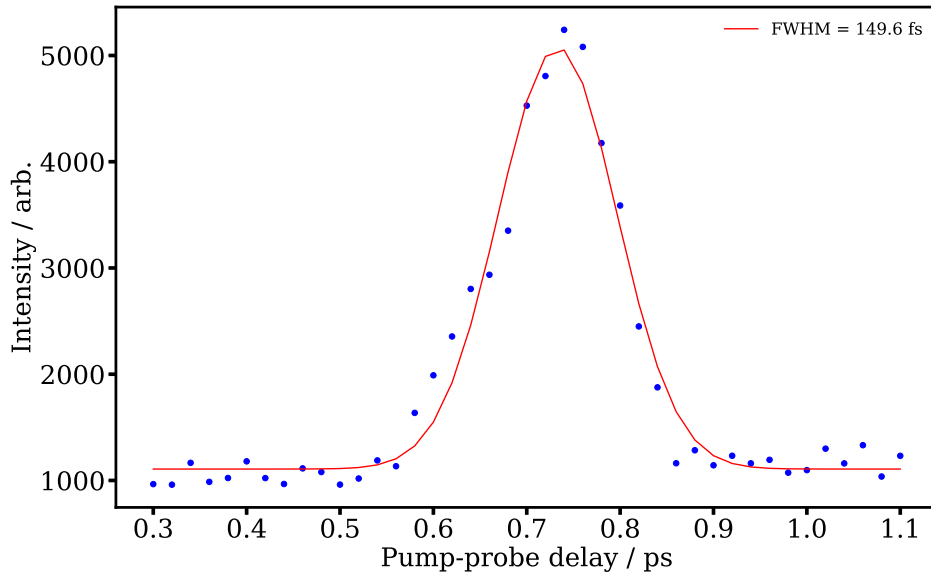


Figure 6.2: The measured cross-correlation between the utilised 201.5 nm pump pulse, and an IR pulse in Xe.

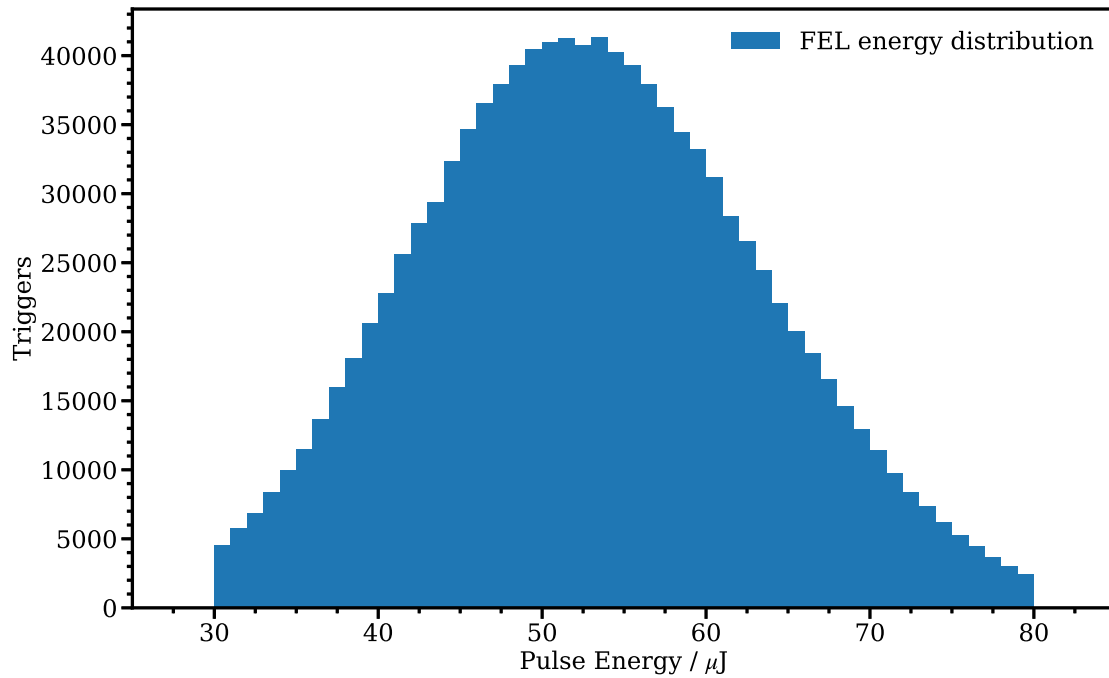


Figure 6.3: Distribution of FEL pulse energies recorded throughout the data collected in the experiment. The data was cropped to between 30 - 80 μJ to help mitigate any unexpected dynamics that could occur at very high or low probe energies.

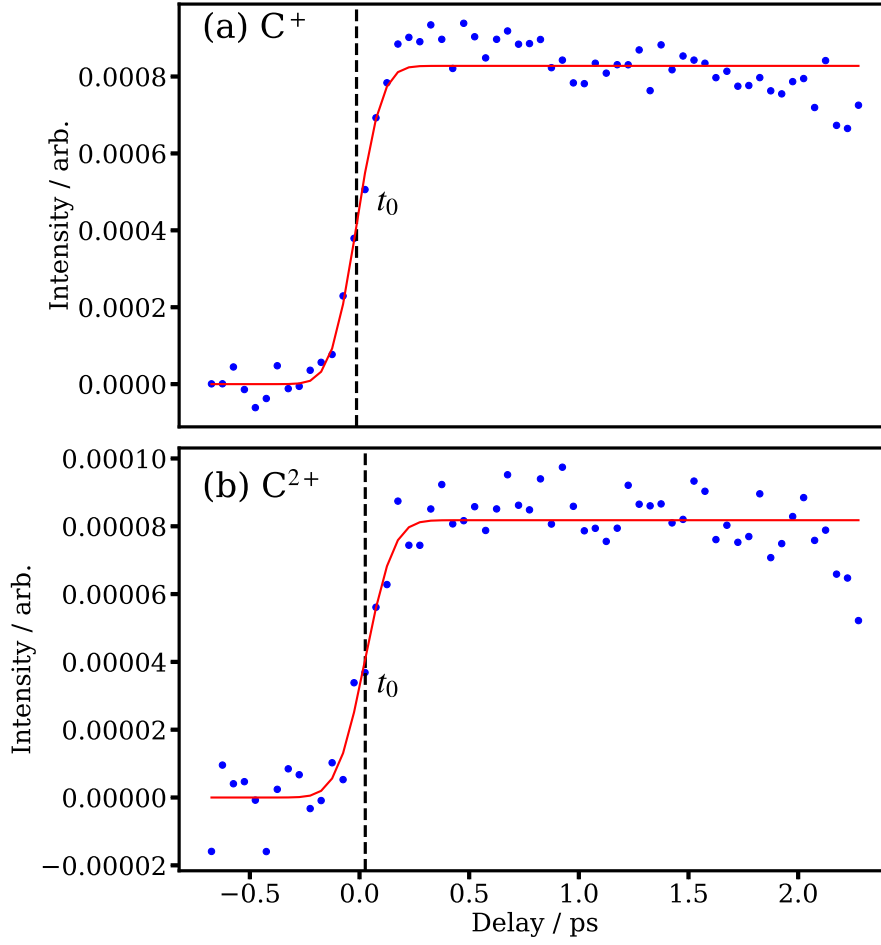


Figure 6.4: Signal enhancement in the C^+ and C^{2+} ions used to determine the temporal overlap point of the two pulses.

133]. ‘LOLA’ reported a soft X-ray pulse duration of 90 fs, which, taking a focal spot size of 10 μm , gives an intensity of $7.2 \pm 1.3 \times 10^{14} \text{ W cm}^{-2}$. Both this probe laser, and the UV pump laser were operated at 10 Hz.

The CS_2 molecules were introduced to the interaction region perpendicular to the laser pulses using a continuous supersonic jet. A drilled aluminium mirror was used to overlap the pump and probe pulses with a near collinear geometry, and the delay period between the two pulses was controlled using a delay stage in the IR path used to generate the pump pulse. The point at which both pulses interact with the sample at the same time, t_0 , was determined using the onset time of a signal enhancement visible in the C^+ and C^{2+} ions, which is shown in Figure 6.4.

After the CS_2 molecules interact with the pump and probe pulses, ion optics

with velocity map imaging potentials are used to direct any produced ions onto a position-sensitive detector consisting of two microchannel plates and a P47 phosphor screen. Hits on this screen were recorded using a Timepix3 camera, the properties of which are discussed in Chapter 3. The resolution of these hits was improved via centroiding according to the method outlined by Bromberger *et al.*[91]

6.3 Results and Discussion

Multiple different fragments were recorded by the TimePix camera per laser shot. These included both time-independent fragments and time-dependent fragments. Various S^{1-4+} , C^{1-2+} and CS^{1-2+} ions were detected. Figure 6.5 displays three mass spectra for the collected data, showing the observed ions for the UV and soft X-ray pulses on their own, and the effect of having the UV pulse precede the soft X-ray pulse. The above mentioned ions are all visible, with a noticeable increase in intensity of the sulfur states, $S^{>1+}$, when the UV pulse arrives before the X-ray pulse. This is most noticeable in S^{2+} . The majority of the parent ion observed is attributed to two-photon ionisation of the ground state parent of CS_2 .

6.3.1 Time-Independent Data

For each of the ions described above, 3D momentum distributions were produced that show ion intensity as a function of momentum against pump-probe delay. These distributions are shown in Figure 6.6. In each panel in Figure 6.6, a strong signal with constant momentum is seen, consistently at higher momentum than the signals that show time dependence (for the sulfur ions). These constant momenta signals are attributed to events where the soft X-ray pulse interacts with the molecule prior to the UV pulse, and hence prior to any excitation occurring. Since no excitation occurs in these events, no subsequent dissociation occurs. Therefore these signals are simply the result of the soft X-ray pulse multiply ionising the ground-state parent CS_2 molecule, which proceeds to fragment into highly-charged fragments. The time-independent signals in the sulfur ions are observed at higher momenta than the time-dependent signals due to the geometry changes that occur during

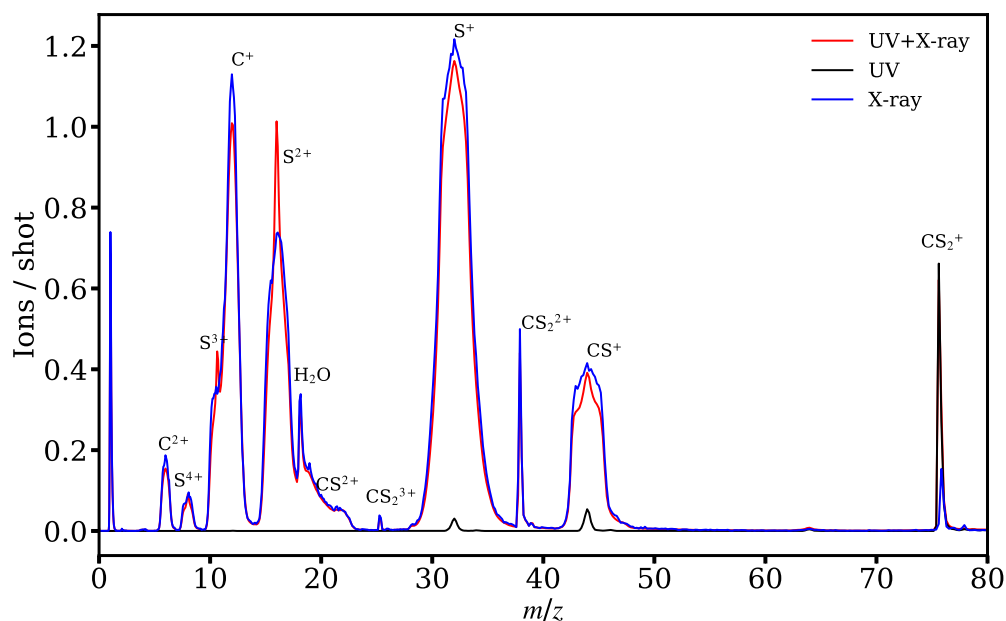


Figure 6.5: Mass spectra for the three different laser pulse combinations: UV-only, soft X-ray-only and UV+soft X-ray. UV+soft X-ray data only includes data for which the UV pulse precedes the X-ray pulse. S^{1-4+} , C^{1-2+} , CS^{1-2+} and CS_2^{1-2+} are all observed.

dissociation. These structural changes lead to a greater proportion of fragment momentum being partitioned into the carbon ion, and consequently leads to the time-dependent sulfur features having less momentum. This will be visible in the 3D momentum distributions shown later in this Chapter.

6.3.2 Time-Dependent Data

Of more interest in this thesis are the time-dependent signals observed in the various recorded ions. A time-dependent mass spectrum is shown in Figure 6.7, which provides signals at each m/z ratio, as a function of pump-probe delay. Any signals arising from X-ray only interactions were removed by subtracting the average signal obtained for each ion between a pump-probe delay of -0.7 to -0.2 ps, chosen to provide an accurate representation of the X-ray only data. This makes it considerably easier to view any enhancements or depletions that result from the pump-process. Enhancements in S^+ , S^{2+} , S^{3+} , S^{4+} , C^+ and C^{2+} are seen when the UV pulse precedes the X-ray. Also seen are depletions in the multiply charged parent ions.

The same subtraction process (removing an average of the data from -0.7 to

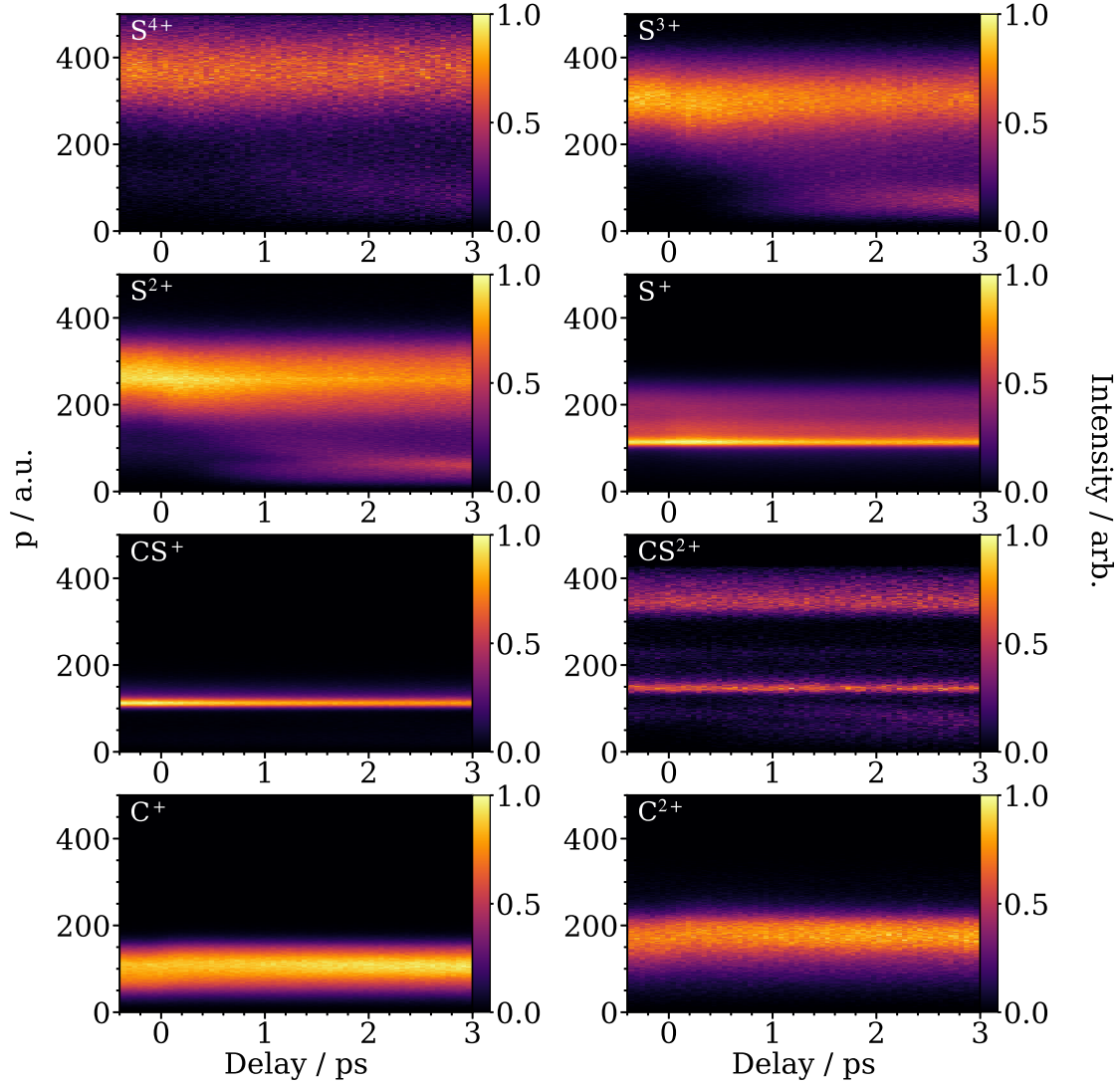


Figure 6.6: Full time-resolved momentum distributions for all CS_2 ions detected. Shown are S^{1-4+} , C^{1-2+} and CS^{1-2+} .

-0.2 ps) used to generate Figure 6.7 can be applied to the momentum distributions in Figure 6.6. This produces 3D momentum distributions that highlight any enhancements resulting from a UV excitation prior to probing. Figures 6.8 and 6.9 show the results of this subtraction. Red signal corresponds to a positive enhancement, and indicates that the shown ion exists after t_0 , while blue corresponds to a depletion, and indicates that the signal has been removed by the subtraction, and therefore is the result of an FEL-only process.

The majority of the discussion hereafter will largely focus on the S^+ , S^{2+} and C^+ ions shown in Figure 6.8, as these ions allow a full accounting of the time-dependent

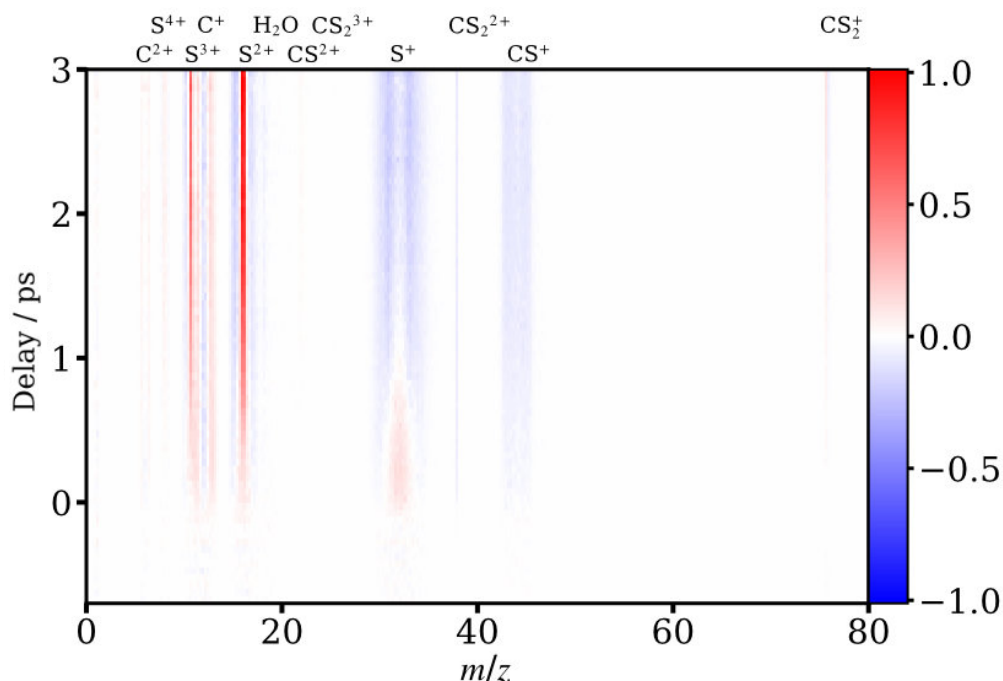


Figure 6.7: Time-dependent mass spectrum showing the UV-early signals of all ions.

dynamics of CS_2 to be completed. To aid in the disentanglement of the multiple overlapping fragmentation channels in each ion, the experimental data was compared to that produced by a simple model, the construction of which is described below.

6.3.3 CEI Modelling

The dynamics occurring before, during and after photoexcitation were analysed by comparison to a set of simulated Coulomb explosions. The following section will describe the process for generating the simulations. Figure 6.10 shows a simplified flowchart of the process used to produce these simulations, with each step expanded upon in detail below.

Initially, a chosen number of molecules were modelled to proceed through the excitation and dissociation processes. For this, an exponential time constant for the dissociation of 500 fs was used, and the excitation was considered to occur promptly. This time constant was chosen based on previous measurements by Farmanara and Townsend of 380 ± 20 fs at 200.7 nm, and 510-640 fs at 201.3 nm[120, 125]. 10,000 molecules were used for these simulations, as this provided the best overlap between

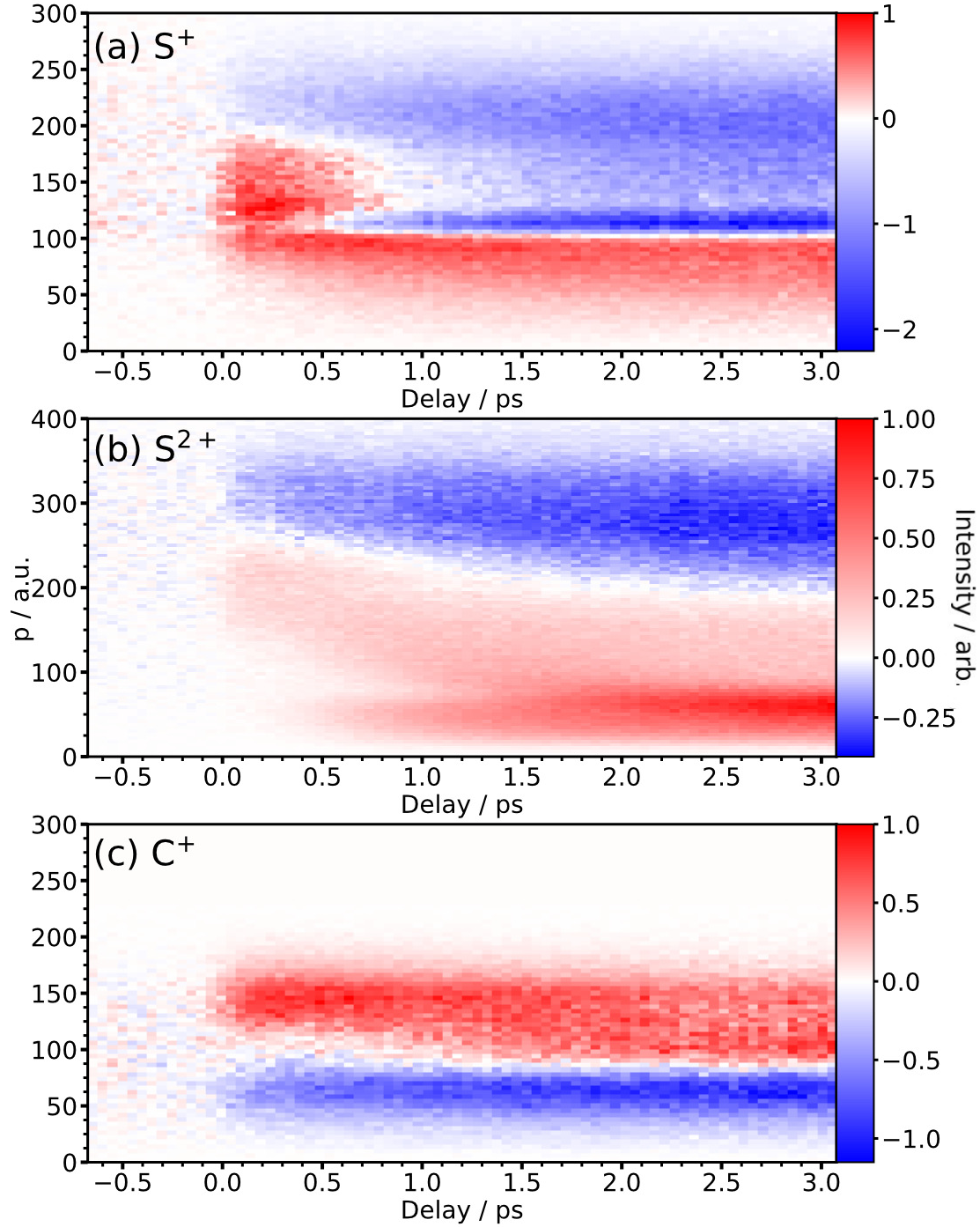


Figure 6.8: Time-dependent background-subtracted momentum distributions of the S^+ , S^{2+} and C^+ ions. Time-independent XUV only signal is removed by subtracting an average of the pre- t_0 signal.

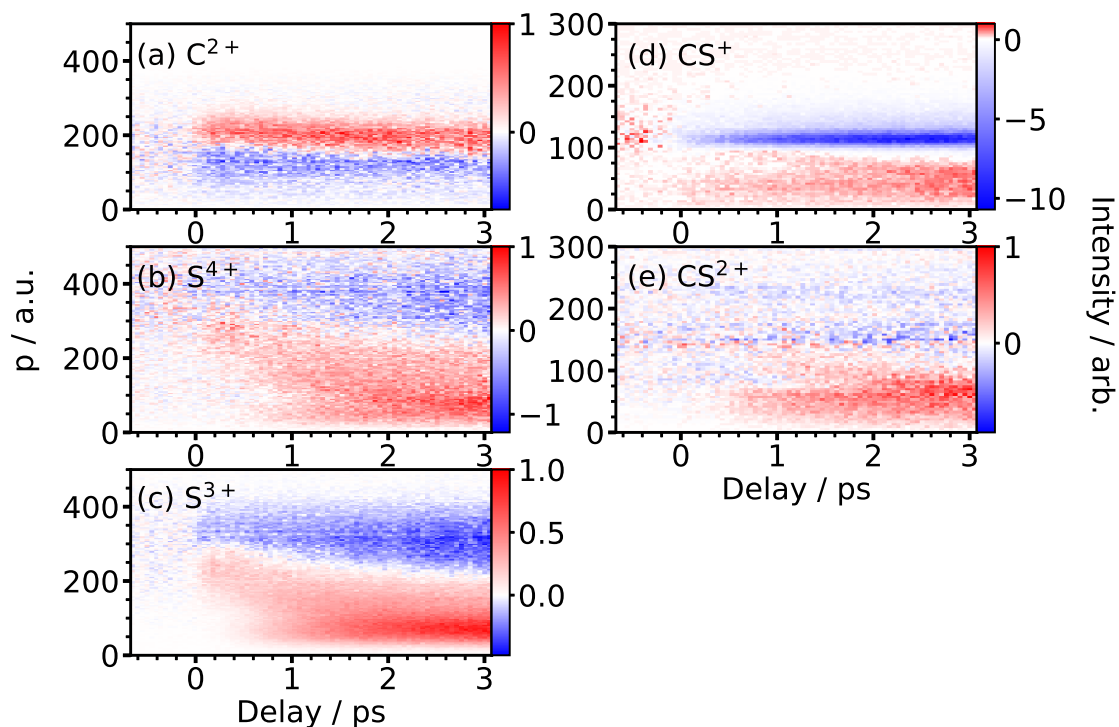


Figure 6.9: Time-dependent background-subtracted momentum distributions of the C^{2+} , S^{3+} , S^{4+} , CS^+ and CS^{2+} ions. Time-independent XUV only signal is removed by subtracting an average of the pre- t_0 signal.

high statistics while keeping computing time reasonable. Figure 6.11 shows the modelled excited- and dissociated-state populations using the above values.

The system was simulated from -500 to 3400 fs, and for each of the above molecules, the geometry was modified to one of three possible combinations, depending on the simulated delay time. This had the effect of accounting for the three different situations a CS_2 molecule could exist in: either the unpumped ground state, the excited, but bound state, or the final dissociated state. The geometries possessed a broad uncertainty to account for neighbouring excited-states of similar energy. For each iteration through the simulation the geometry was randomly sampled from a Gaussian distribution of the geometry for each of the bound, excited and dissociated configurations, with the uncertainty of the value corresponding to the width of the Gaussian distribution. This random sampling of the geometries was chosen to produce an ensemble due to the large number of overlapping and similar excited states. The geometries obtained via sampling a Gaussian distribution are

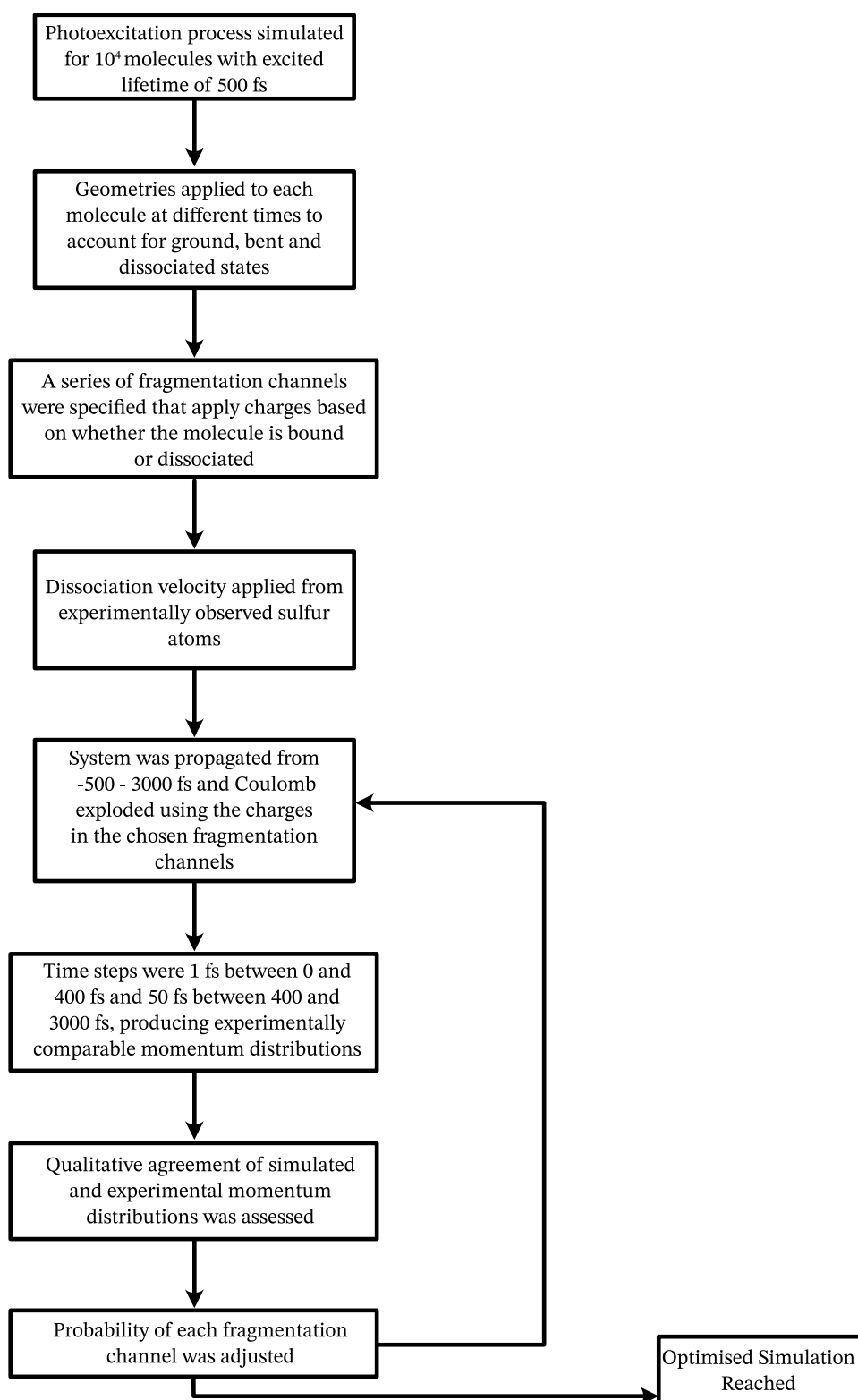


Figure 6.10: Flowchart of the main steps used to produce the simulated CS₂ momentum distributions.

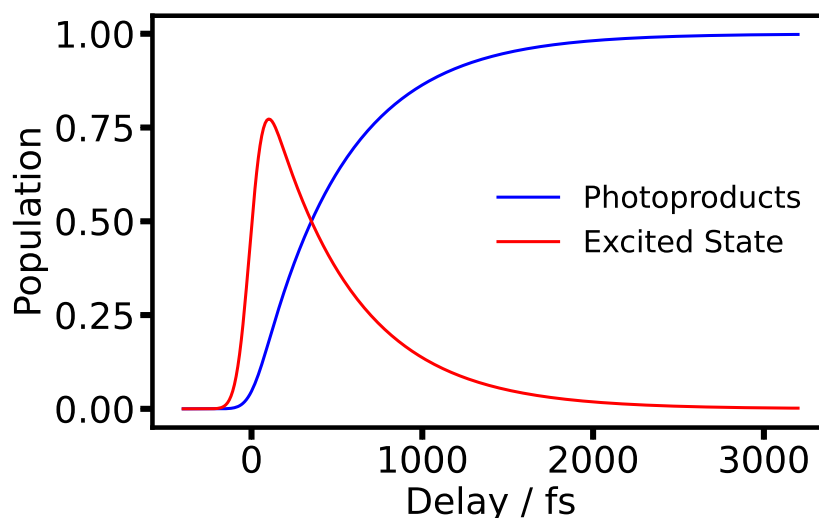


Figure 6.11: Simulated excited- and dissociated-state populations of CS₂ prior to Coulomb explosion.

sufficient for the analysis within this thesis without necessitating the computational requirements, time and high-level theory to accurately calculate PESs for each individual state. The geometries used to describe the three states are shown in Table 6.1, and were determined using a combination of experimental and existing theoretical values. The bend angle and dissociation velocities were determined from the experimental covariance and Gaussian kinetic energy distribution of the dissociated sulfur atoms, respectively. This bend angle was extracted from the covariance data by plotting the covariance image of the total recoil-momenta of the two sulfur atoms as a function of their angle, and fitting a Gaussian distribution to the integrated intensity of this signal (shown in Section 6.3.4 in Figure 6.17). This dissociation velocity also allows the determination of the amount of rotational energy possessed by the CS fragment. For the ground state, an angle of $<180^\circ$ was used, as determined by Hasegawa *et al.*[115].

A number of fragmentation channels were specified, to account for the different possible charge states after interaction with the soft X-ray probe. The total number of channels were kept to a minimum, to provide as good an agreement with the experimental data as possible, without needlessly increasing the complexity of fitting the channels. Each of these channels possessed two sets of charge states, accounting

Table 6.1: Structural parameters used in the Coulomb explosion simulations.

Parameter	Mean $\pm$ Standard Deviation
Equilibrium C-S length	$1.55\text{\AA} \pm 0.1\text{\AA}$ [115]
Equilibrium S-C-S angle	$165.5^\circ \pm 9^\circ$
Excited, bent C-S length	$2.2\text{\AA} \pm 0.5\text{\AA}$
Excited, bent S-C-S angle	$135^\circ \pm 40^\circ$
Dissociated C-S length	$1.8\text{\AA} \pm 0.4\text{\AA}$

for the probing of the molecule at short S-CS separation, ‘bound’, and at large S-CS separation, ‘dissociated’. This was due to the possibility of charge transfer at short delays. This R_{crit} value was assigned to $5.5\text{ \AA}$, which corresponds to an approximate average of the value predicted via the OTB model for charge transfer from a variety of singlet and triplet sulfur atoms (Table 6.3 later in the analysis). These channels enabled the Coulombic velocity of the experiment to be included with the dissociation velocity, and provide a description of the momentum of each fragment. Each channel assigned classical point charges to each atom in the CS_2 molecule, which Coulombically repelled. Where there was a neutral fragment, and hence point charges are inaccurate, a partial positive charge (sampled uniformly between 0.05 and 0.3+) was applied to the neutral. The resultant momenta of the fragments after applying these charges were calculated by solving classical Newton equations using the `solve_ivp` function from `SciPy`, across the same delay range as the experimental data[134]. At short delays after t_0 , and hence during the time period where the bending dynamics were expected to occur, timesteps of 1 fs were used, while at longer delays, to account for the expected lack of geometry change after dissociation, broader time steps of 50 fs were applied. This variation in time step at later delays greatly decreased the compute time to model the system.

The combination of these fragmentation channels, along with the photodissociation dynamics described above, allowed the full momentum distributions to be simulated. For each of the 10,000 molecules a fragmentation channel was assigned, using manually specified probabilities given to each channel. The charges specified by the channel were applied to the molecule at each delay point, and as such, were applied to the molecule in the different geometries described above, depending on

Table 6.2: Fragmentation channels specified for the Coulomb explosion simulations. These are specified by charges (m,n,p) for three-body Coulomb explosions of either S_a-C-S_b (bound) or S_a+CS_b (dissociated) into S_a^{m+}+Cⁿ⁺+S_b^{p+} and charges (q,w) for two-body Coulomb explosion into S^{q+}+CS^{w+}. Channel probabilities were determined by empirical fitting. S_a corresponds to the sulfur atom where the S-C bond is cleaved, while S_b corresponds to the sulfur that remains bound to the carbon.

No.	Bound $(q,w)/(m,n,p)$	Dissociated (m,n,p)	Probability (%)
1	(1,1)	(2,0,0)	12.5
2	(1,1,1)	(0,1,2)	17.5
3	(2,1,1)	(2,1,1)	15.0
4	(2,1,2)	(2,1,2)	7.5
5	(2,0,1)	(3,0,0)	10.0
6	(1,0,1)	(2,0,0)	5.0
7	(1,1,0)	(0,0,2)	5.0
8	(1,1)	(0,1,1)	15.0
9	(1,0,1)	(0,1,1)	7.5
10	(1,1,1)	(3,0,0)	5.0

the delay value. This produced a full momentum distribution for each charge state that was then convolved with a Gaussian function of $\sigma = 50$ fs to simulate the experimental time resolution. Plotting these momentum distributions enabled the probability of each fragmentation channel to be adjusted to produce the optimal overlap with the experimental data. It is worth noting that any valence ionisation, or production of stable CS²⁺ are not accounted for in this simulation. It is also worth noting, that due to their similarity in features to S²⁺, and their comparatively low statistics, many S³⁺ and S⁴⁺ channels were excluded.

It was found that optimal agreement with the experimental data was achieved with ten fragmentation channels. These ten channels, and their corresponding probabilities, are shown in Table 6.2.

For each ion of S⁺, S²⁺ and C⁺, each individual channel can be plotted, with their intensity scaled to account for the varying probability. Summing each of these channels gives a total simulated momentum distribution for each ion. Figures 6.12, 6.13 and 6.14 show the individual contributions of each channel to each ion, and their summed momentum distributions. To remove the data where the molecule is in its ground state, the average of the signal preceeding t_0 was removed.

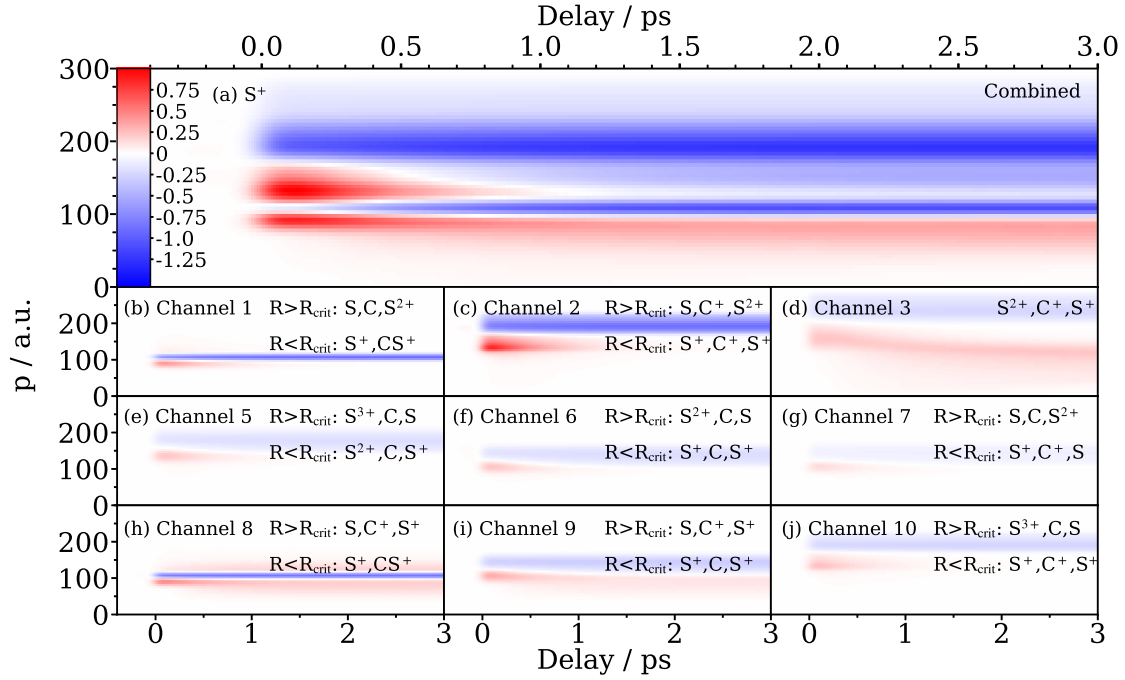


Figure 6.12: The individual channels which contribute to producing the S^+ simulated momentum distribution. Panel (a) shows the combined simulation, while (b)-(j) show the individual channels, produced using the charges and probabilities specified in Table 6.2. The channels with a higher probability of occurring show as regions of more intense signal, with more infrequent charge distributions appearing fainter. Negative signal corresponds to simulated depletion of the ground-state molecule, with enhancements corresponding to excitation.

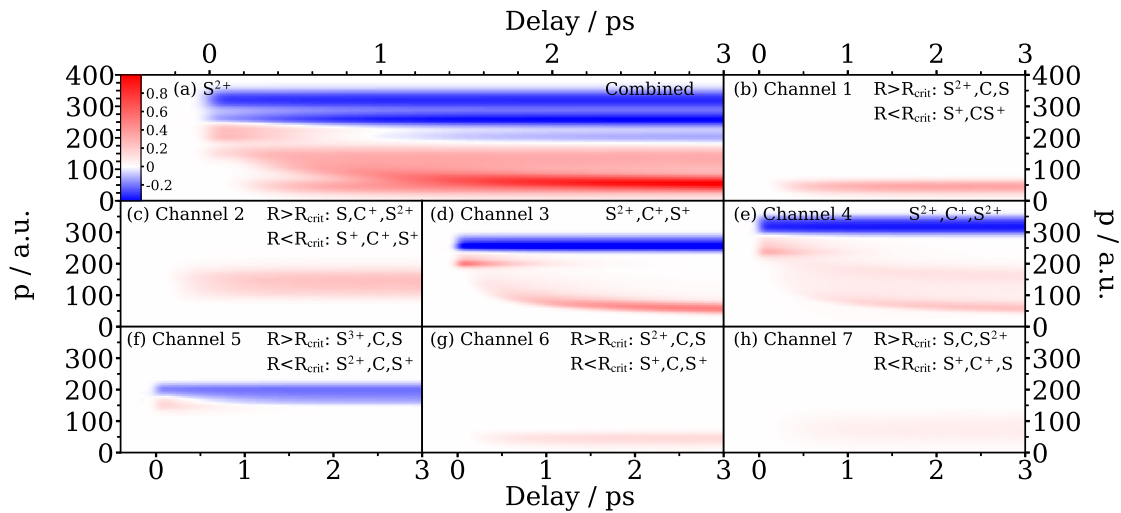


Figure 6.13: The individual channels which contribute to producing the S^{2+} simulated momentum distribution. Panel (a) shows the combined simulation, while (b)-(h) show the individual channels.

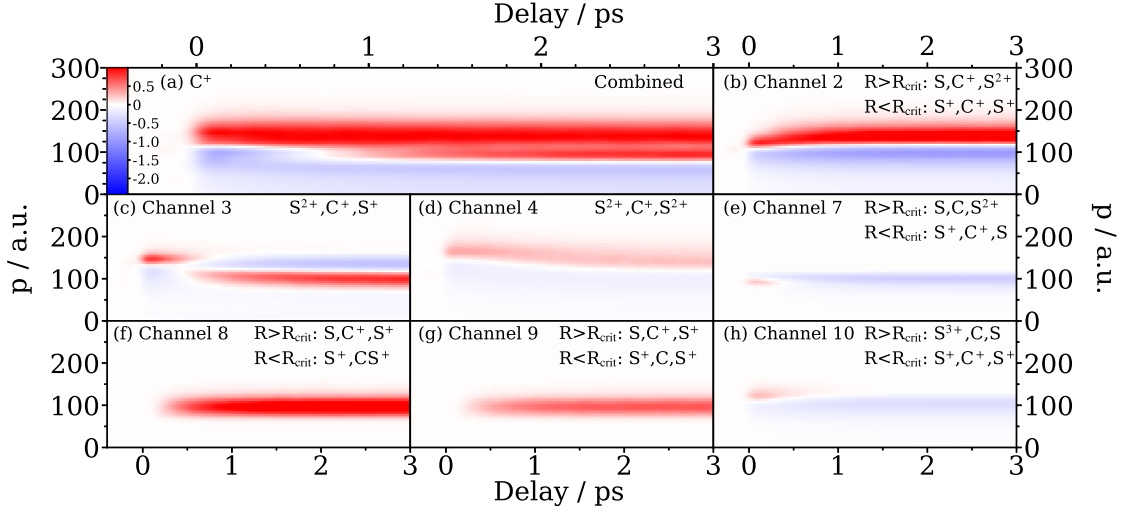


Figure 6.14: Individual channels which contribute to producing the C^+ simulated momentum distribution. Panel (a) shows the combined simulation, while (b)-(h) show the individual channels.

Each simulated momentum distribution was optimised by manually adjusting the channel probability, number of channels, charge distribution, bend angle, bond length and R_{crit} value until strong agreement with the experimental data was obtained and no significant further improvement was accomplished. To show the effect each parameter has on the simulated momentum distributions, examples are given in Appendix A, which show the extreme outer limits of the tested values, corresponding to significant changes in each parameter. This is intended to allow the reader to see the types of changes that occur in individual features when the simulation parameters are adjusted, and therefore give an indication as to how the final optimised simulations were reached. How each of the parameters were adjusted are as follows: for channel probability the five most likely channels had their probability decreased by 0.1, with the five least likely channels having their probability increased by 0.1 (so as to maintain a 100% channel selection rate). For the number of channels, the total number of included channels was decreased to only utilise the five most likely channels. For adjusting the charge distribution within each channel the charges on each atom were rearranged so that the total charge state of the molecule remained unchanged, but different atoms possessed different charges. For the bond lengths and angles between atoms, each was increased and

decreased by 20%, respectively. Finally the critical distance value was increased and decreased to 10 Å and 2 Å, respectively.

6.3.4 S⁺ Analysis

Momentum Distribution

Starting with the S⁺ ion signal, Figure 6.15 shows the experimental S⁺ data, compared to the optimised simulated S⁺ data. The chosen X-ray wavelength (tuned to be just above the S 2p edge), largely precludes the production of singly charged sulfur ions from the ionisation of dissociated sulfur atoms, as Auger decay eliminates a minimum of two electrons. This means that, instead of the S⁺ products being the result of direct soft X-ray ionisation of the sulfur atom, instead they are formed from charge redistribution after ionisation of the bound excited molecule, or the produced CS fragment after dissociation. This gives some initial indication as to the possible formation pathways of the S⁺ signal.

Therefore, starting with the experimental data, there are several distinct signals. These are an enhancement from ~60-100 a.u. that extends across all positive delays, which is assigned to the two-body explosion at short delays, or the explosion of a dissociated CS fragment at longer delays, and a shorter-lived transient signal between 110-180 a.u., which is attributed to the explosion of excited, bent CS₂. These assignments will be validated below using the simulated distribution as well as covariance analysis.

The optimised S⁺ simulation comprises nine different S⁺ producing reaction channels, as described in Table 6.2. Strong qualitative agreement can be seen between the experimental and simulated momentum distributions, with signals of similar intensities present at similar delays and momenta. This enables the composition of the reaction channels in the simulated distributions to correlate to the composition of the experimental distribution. As such, the transient enhancement between 110-180 a.u. in the experimental data is primarily the result of the excited ‘bound’ (1,1,1), (2,1,1) and (2,0,1) channels prior to dissociation into an isolated sulfur atom (Channels 2, 3, 5 and 10), with some more minor contributions from

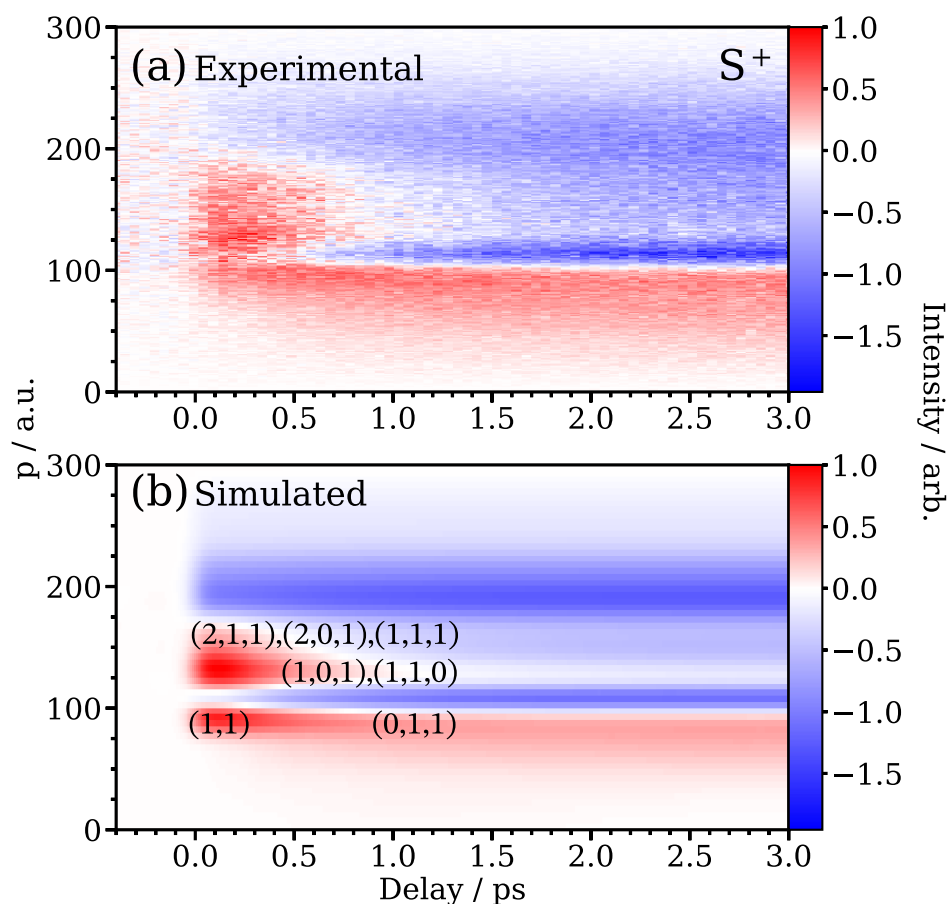


Figure 6.15: Comparison of the experimental subtracted S^+ momentum distribution to the optimised simulated S^+ momentum distribution. Labelled in panel (b) are the simulated reaction channels corresponding to each signal.

$(1,0,1)$ and $(1,1,0)$ (Channels 6 and 7). As a reminder, (m, n, p) corresponds to the charges on the corresponding atoms with m being the sulfur where the C-S bond is cleaved, n being the carbon, and p is the sulfur that remains bonded to the carbon. As mentioned earlier, the lower momentum of this signal compared to the ground state makes sense due to the increased bending of the molecule causing a greater carbon momentum. The lengthening of the S-C bonds also decreases the Coulombic contribution.

Turning to the more constant, lower momentum signals between 60-100 a.u., at short delays these are assigned to the $(1,1)$ channel (Channels 1 and 8), corresponding to a two-body fragmentation into S^+ and CS^+ . At longer delays they instead are assigned to the dissociated CS fragment exploding into S^+ and C^+ ($(0,1,1)$, Channels

8 and 9). A large range of C-S bond lengths is expected to exist for a vibrationally hot CS fragment, and so applying this to the simulation (the utilised dissociated C-S length in the simulation was $1.8 \text{ \AA} \pm 0.4 \text{ \AA}$, as in Table 6.1) again produces a strong agreement to the experimental data, and validates the assignment of this signal arising from CS explosion.

Covariance Analysis

While the momentum distributions were sufficient to confirm the existence of a bent, transient, excited state, the degree of this bending was characterised using two-fold time-dependent contingent covariance (as described in Section 3.4.4). The covariance was performed using thirty contingent bins with equal statistics per bin, and filtered to remove the upper and lower edges of the FEL energy distribution. This is shown in Figure 6.16. The two-fold covariance was calculated for two ion pairs: (S^+, S^+) and (S^+, C^+) .

Figure 6.17 shows experimental and simulated covariance for the (S^+, S^+) ion pair, along with various plots of the extracted parameters. The type of covariance used here is the one earlier termed recoil-angle covariance (Section 3.4.5), which shows covariance as a function of summed ion pair momenta and recoil angle. This representation was the most logical choice here, given that the main purpose was identifying the bend angle in the excited state. Subtraction of the UV-late signal was performed on this data in the manner as described above, to again remove any contributions from FEL-only interactions. As mentioned in Section 6.3.3, the bend angle determined from the experimental covariance was subsequently used to refine the bend angle utilised by the simulation, and the experimental covariance was then compared to the covariance obtained from the modelled data, to support the linking of the experimental channels to the simulated channels.

The covariance in Figure 6.17 is calculated over a specified time period ($0 < t < 0.7 \text{ ps}$), corresponding to the delay between the pump and probe pulses. This was done due to the relatively low statistics of the dataset prohibiting fine, 100 fs binning, but also because this delay range accounts for primarily probing the bound

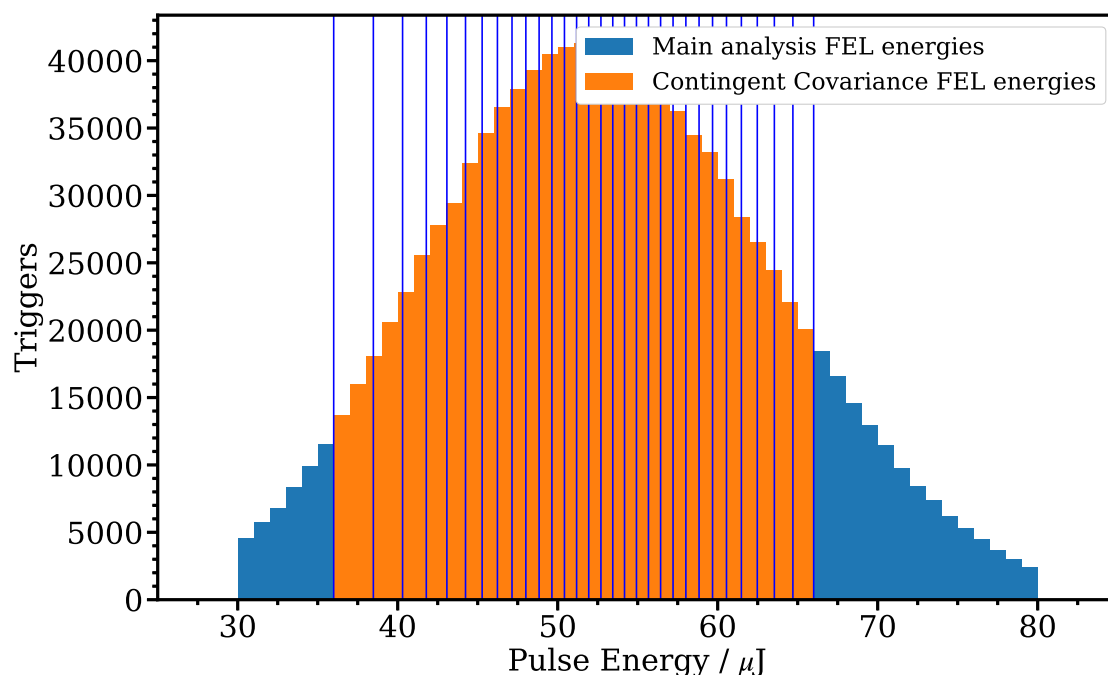


Figure 6.16: FEL energy bins used for the CS_2 contingent covariance calculations.

excited state. Panel (a) shows a strong enhancement centred at $\sim 135^\circ$ and 300 a.u., that is consistent with the signal in the simulated panel (b). Therefore from the model, these signals are primarily assigned to the (1,1,1) and (1,0,1) channels from probing excited bound CS_2 . The momentum projection in panel (c) shows that the recoil angle peaks at $\sim 135^\circ$, giving clear evidence to the degree of bending in excited CS_2 . The momentum of this feature (corresponding to the summed momenta of the two sulfur ions) is also roughly equivalent to the sum of the transient signal seen in the S^+ momentum distribution, which was assigned to the same reaction channel. The broad nature of this feature is consistent with the wide range of bond lengths and angles sampled in the excited state. The experimental and simulated signals in panels (c) and (d) again broadly agree, affirming the assessment that the simulated data includes the key experimental channels, and that the input parameters were well chosen. As mentioned above, the excited state bend angle of 135° determined here was used to improve the accuracy of the simulation. Panel (e) shows the covariance signal as a function of pump probe delay. The integrated regions for this plot are shown in Figure 6.18.

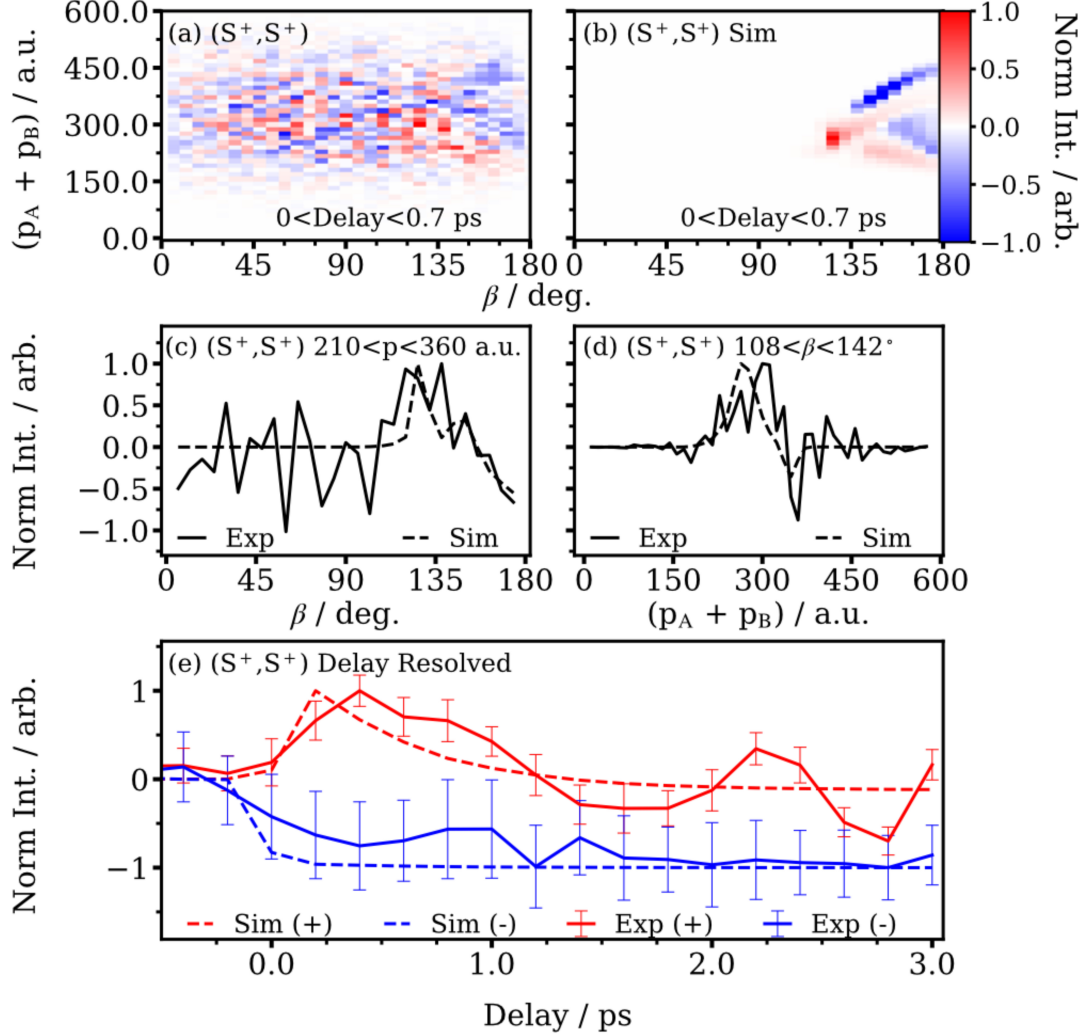


Figure 6.17: Panels (a) and (b) show 3D covariance analysis for the (S^+, S^+) ion pair for the experimental and simulated data, respectively. Data are presented for delays $0 < t < 0.7 \text{ ps}$ between the UV pump and soft X-ray probe to highlight relevant features. The covariance signals are plotted as a function of β , the relative recoil angle of the two ions, and the sum of their absolute momenta in atomic units. Panels (c) and (d) show one-dimensional projections with respect to angle and momentum for both the experimental and simulated data of each ion pair. Panel (e) shows one-dimensional projections of delay as a function of intensity for both the major enhancements and depletions in each experimental and simulated covariance image, with 200 fs delay bins. The time-dependent covariance intensities were normalised to ± 1 for the enhancements/depletions, respectively. The integrated regions of the covariance image used for these time-dependent momentum projections are shown in Figure 6.18. Errorbars were produced via bootstrapping analysis using 100 repetitions of the covariance calculation.

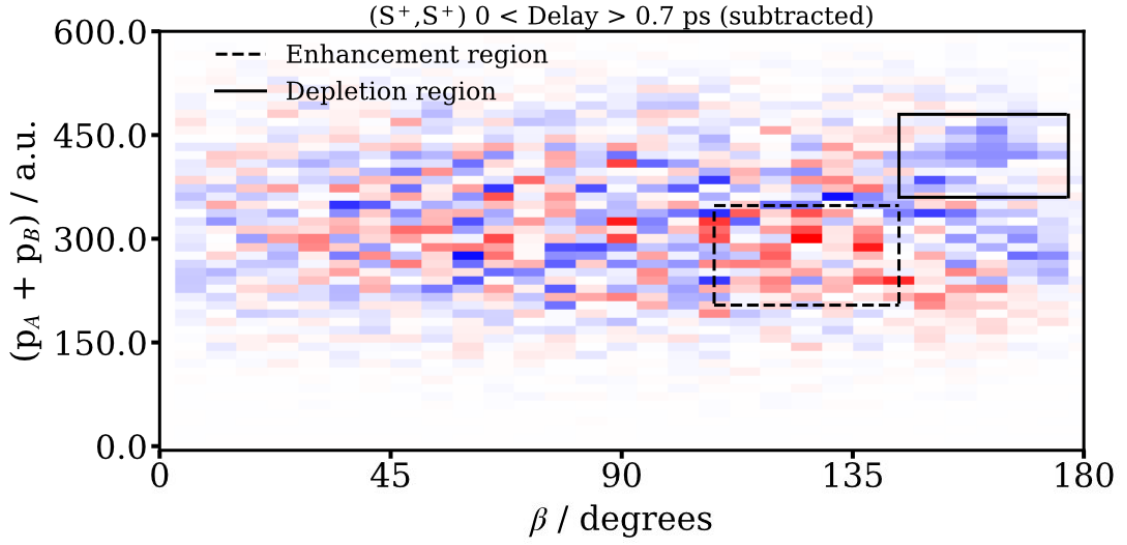


Figure 6.18: Regions chosen to integrate enhancements and depletions over to produce a plot of covariance against pump-probe delay for (S^+, S^+) recoil.

Strong agreements between the experimental and simulated transient enhancements and ground state depletions are also seen. The broader nature of the experimental data compared to the simulation can be attributed to two things: firstly, an experimental limitation, in that there is a maximum resolution distinguishable by the spectrometer. Secondly, the model doesn't account for any gradual charging or Coulombic deviations, when applying the charges to the fragments, or modelling the ultrashort timescales. To conclude the discussion of the (S^+, S^+) covariance, Figures 6.19 and 6.20 show the covariance of the (S^+, S^+) ion pair for delays where $t > 1.7$ ps and the covariance for where the soft X-ray precedes the UV pulse. For Figure 6.19 it can be noted that the enhancement visible at short delays is completely absent. As expected, this further confirms the transient nature of this feature. At later delays the molecule will have fully dissociated, and therefore can no longer exist as bent excited CS_2 . The excitation of the molecule results in a depletion of the ground-state signal. Therefore, in the subtracted covariance images, this is expected to show up as a depletion. Figure 6.20 compares the UV-late covariance images for both the experimental and simulated data, and confirms that for UV-late data, a ground-state enhancement is seen at the same angle and momentum as the depletions in the subtracted data in Figure 6.17.

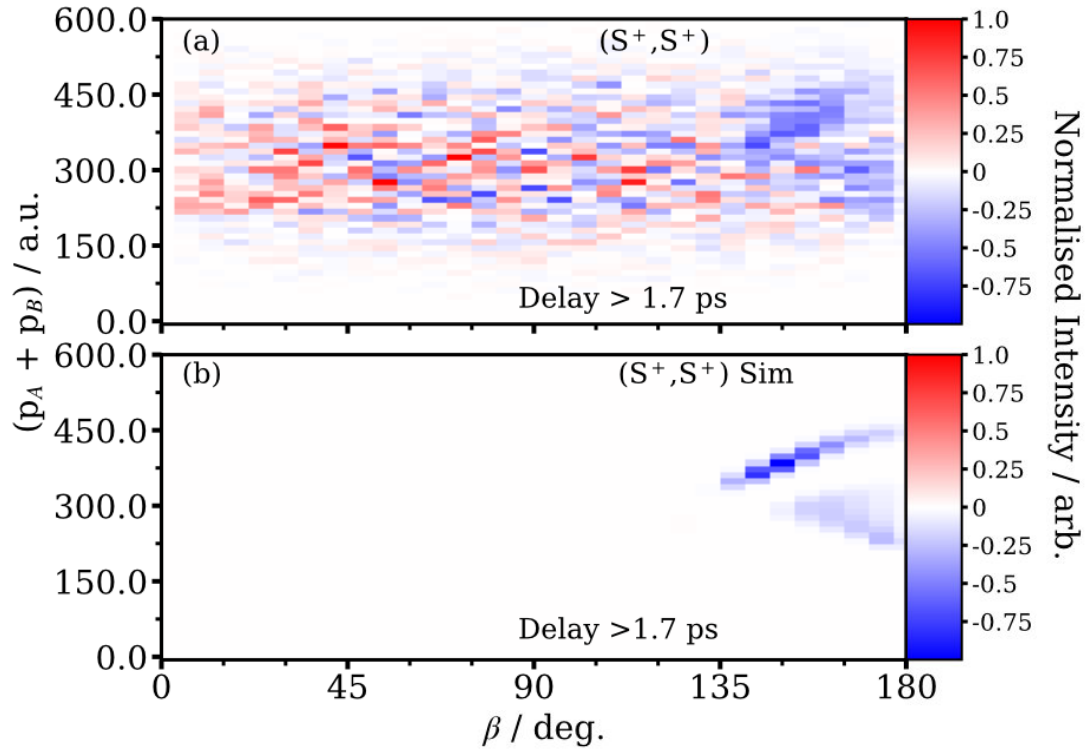


Figure 6.19: (S^+, S^+) covariance for delays where $t > 1.7$ ps.

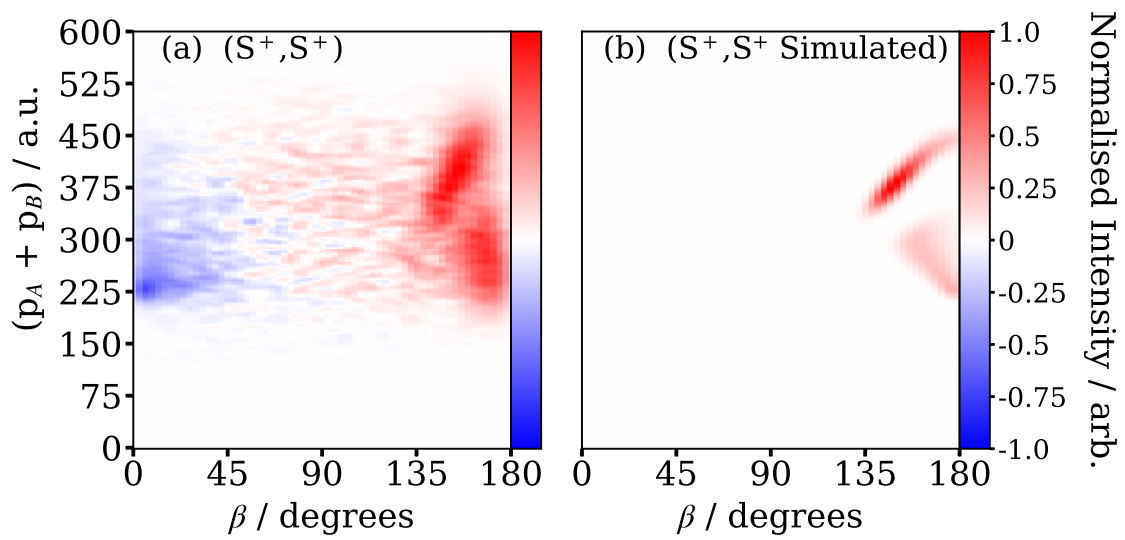


Figure 6.20: Covariance when filtering delays for $t < 0$ ps for (S^+, S^+) recoil.

Turning to the (S⁺,C⁺) covariance, Figure 6.21 shows the covariance images for (S⁺,C⁺) recoil in the same representation as Figure 6.17. Here, the covariance is calculated over a later delay range ($t > 1.7$ ps). A strong enhancement is seen at ~ 225 a.u. and 140 - 180° (confirmed by the plots in Figure 6.21(c) and (d)). This signal was attributed to the Coulomb explosion of a dissociated CS fragment, instead of a bound CS₂ molecule. It would typically be expected that a two-body explosion of the CS fragment would lead to a recoil close to 180° , however, a much broader distribution of angles is observed. This is explained by the possibility of the photodissociation and Coulomb explosion imparting momenta in different directions (as a result of the ground state not being perfectly linear, and hence the photodissociation inducing some rotation of the CS fragment), which results in a broadening of the possible recoil angles. The simulated covariance analysis, which takes a broad recoil angle as an input parameter, supports this assignment. The delay-dependent momentum distributions in Figure 6.21(e) (produced in the same manner as in the (S⁺,S⁺) covariance, and using the integration ranges shown in Figure 6.22) support this assignment, with the signal intensity being low at delays close to t_0 , then gradually increasing in intensity with increasing delay.

This lack of signal at short delays is the result of the majority of the CS₂ molecules still being bound, with the gradual rise caused by a greater proportion of molecules dissociating with greater delay. The momentum distribution of this enhancement covers a fairly wide range of momenta, resulting from a wide range of probed bond lengths, due to the high quantity of vibrational excitation after dissociation[135, 136]. Conveniently, this enhancement is more easily distinguished (compared to (S⁺,S⁺) recoil) from the single-colour depletions resulting from the soft X-ray interacting with the ground state CS₂ prior to interaction with the UV-pulse. The main contributor to these drastically different signals is the different recoil angles of the two processes. For signals arising prior to interaction with the UV-pulse, a depletion centred at 100° is seen, while the recoil is closer to 180° for signals after dissociation (as described above). The varying distribution of these two signals can be seen more clearly in the momentum projections in

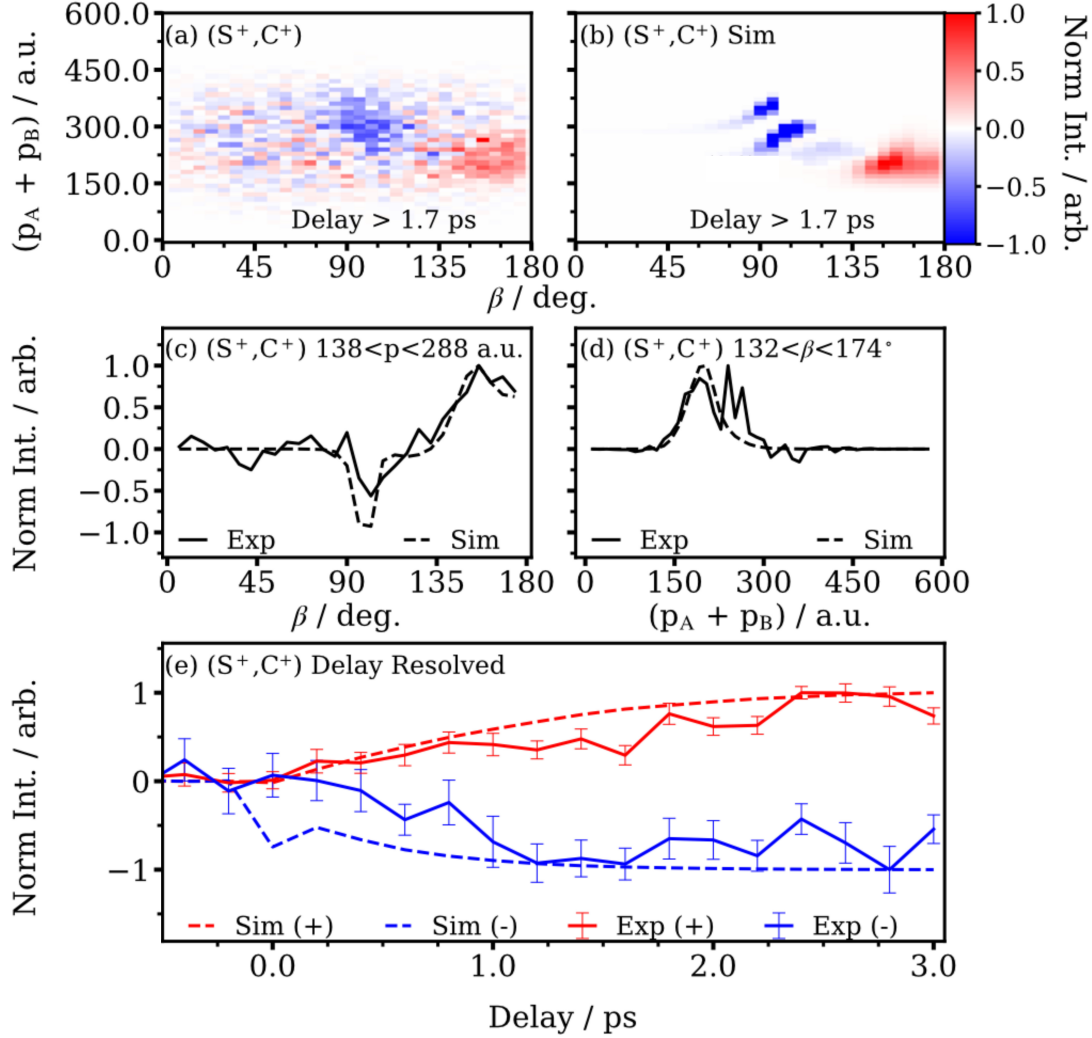


Figure 6.21: Panels (a) and (b) show the three-dimensional covariance analysis for the (S^+, C^+) ion pair performed for the experimental and simulated data, respectively. Data are presented for delays $t > 1.7$ ps between the UV pump and soft X-ray probe to highlight relevant features. The covariance signals are plotted as a function of β , the relative recoil angle of the two ions, and the sum of their absolute momenta in atomic units. Panels (c) and (d) show one-dimensional projections with respect to angle and momentum for both the experimental and simulated data of each ion pair. Panel (e) shows one-dimensional projections of delay as a function of intensity for both the major enhancements and depletions in each experimental and simulated covariance image. The integrated regions of the covariance image used for these time-dependent momentum projections are shown in Figure 6.22. The time-dependent covariance intensities were normalised to ± 1 for the enhancements/depletions, respectively. Errorbars were produced via bootstrapping analysis using 100 repetitions of the covariance calculation.

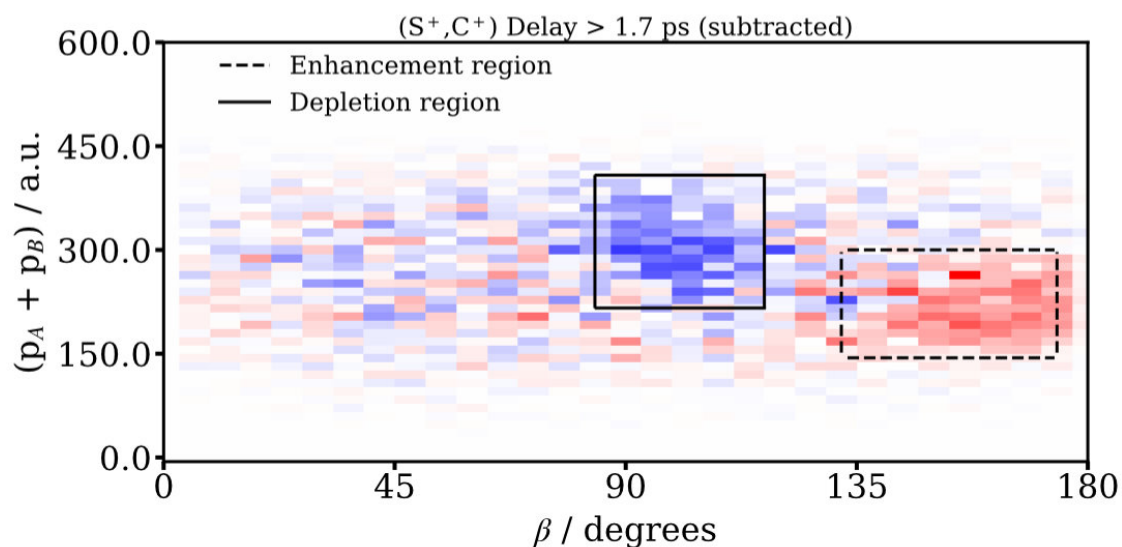


Figure 6.22: Regions chosen to integrate enhancements and depletions over to produce a 1D plot of covariance against pump-probe delay for (S^+, C^+) recoil.

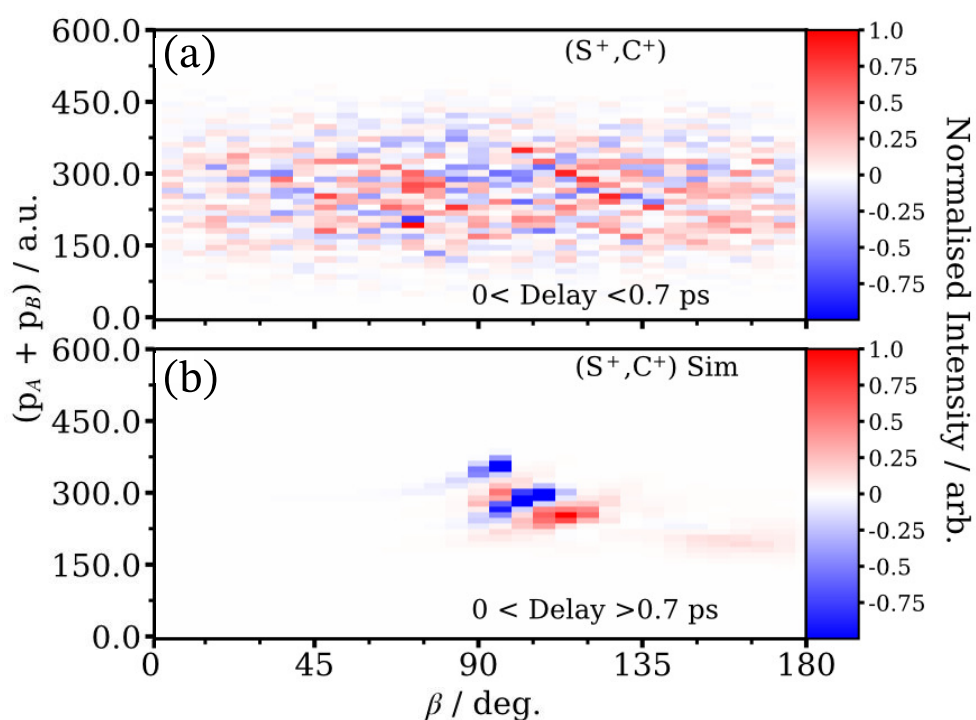


Figure 6.23: (S^+, C^+) covariance for delays where $t < 0.7$ ps.

Figure 6.21(c) and (d). The difference in the delay-dependent depletion at short delays in Figure 6.21(e) is the result of the ground state CS_2 molecule overlapping with excited CS_2 . These two species are more clearly isolated in the simulated data compared to the experimental (Figure 6.23).

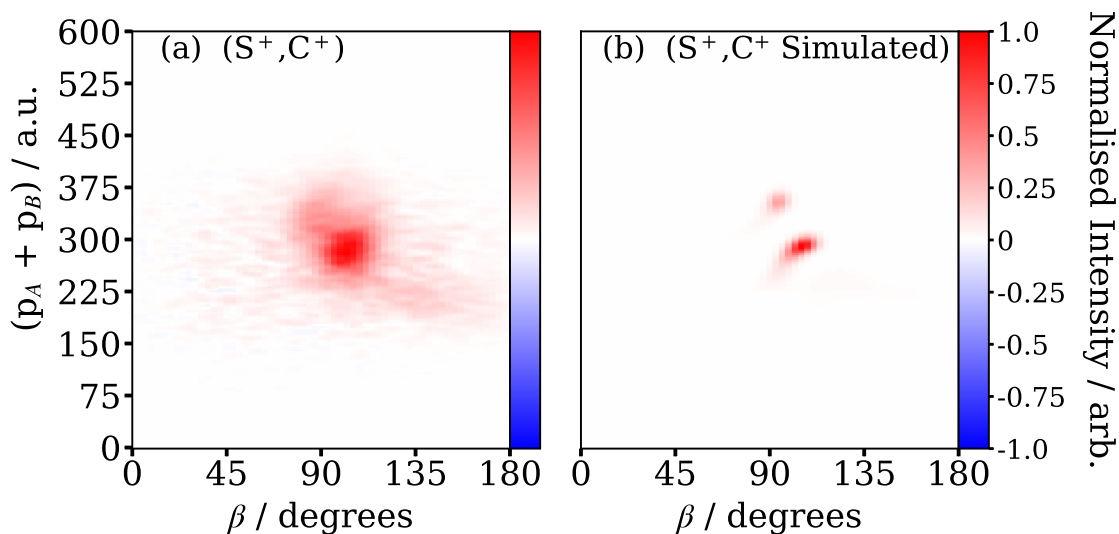


Figure 6.24: Covariance when filtering delays for $t < 0$ ps for (S^+, C^+) recoil.

Figure 6.23 shows the covariance for (S^+, C^+) recoil at short delay values ($t < 0.7$ ps), and, as well as the clearer isolation of the ground and excited signals, shows an absence of the signal at 180° seen at later delays. This supports the assignment of that signal resulting from probing of the dissociated CS fragment, as at shorter delays the majority of the molecules are still bound, and so Coulomb explosion of the bound CS_2 is the dominant channel.

Similar to Figure 6.20, Figure 6.24 gives the covariance analysis for (S^+, C^+) recoil where the soft X-ray probe pulse arrives prior to the pump pulse, and confirms probing of the ground state is the origin of the depletions seen in Figure 6.21(a) and (b).

The strong agreement between the simulated and experimental covariances in Figures 6.17 and 6.21 support the choice of input parameters used in the simulations, and hence the subsequent feature assignment using said simulated data.

6.3.5 S^{2+} Analysis

The momentum distribution for the S^{2+} ion shows considerably different features compared to S^+ . Figure 6.25 shows both the experimental and simulated S^{2+} distributions. The primary cause of these differences is the difference in how the $1+$ and $2+$ charge states are obtained. As mentioned above, the majority of the S^+ signal is not produced from direct ionisation of dissociated sulfur, and

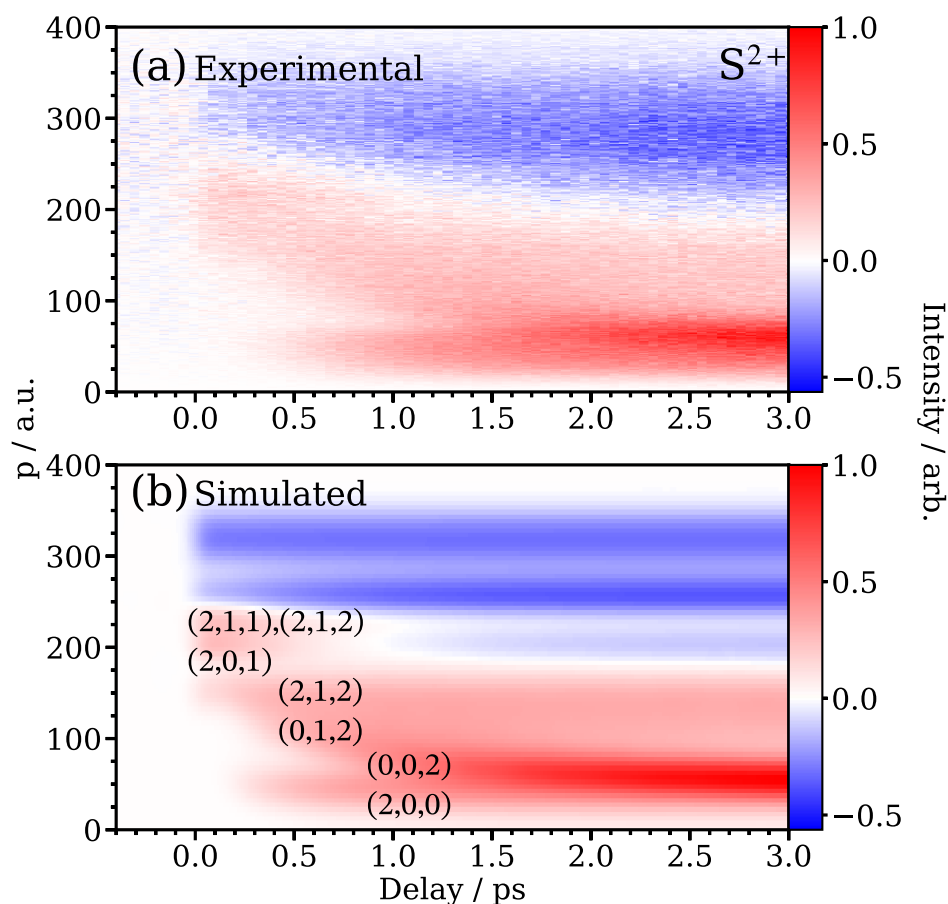


Figure 6.25: Comparison of the experimental subtracted S^{2+} momentum distribution to the optimised simulated S^{2+} momentum distribution. Labelled in panel (b) are the simulated reaction channels corresponding to each signal.

instead from charge redistribution. Conversely, due to the FEL wavelength being tuned to ionise above the S 2p edge, in the S^{2+} momentum distributions signal can be observed from direct ionisation of dissociated sulfur to a 2+ charge state. From Table 6.2 and Figure 6.13, it can be seen that the momentum distribution is made up of seven main reaction channels, which can be grouped into several main features. These features are also present in the S^{3+} and S^{4+} distributions, and they can be assumed to originate in the same manner, albeit with higher momentum due to greater Coulombic repulsion.

Firstly, within the first picosecond following excitation, a positive transient signal is seen between 190-250 a.u., akin to that seen in Figure 6.15. This feature shows the same lifetime as that in S^+ , and it arises from probing while in a bent

excited state (again akin to the S^+ feature). The higher momentum of this feature compared to that in S^+ is easily explained by a greater Coulombic component, due to the presence of a $2+$ versus $1+$ charge. Looking at Figure 6.13, it can be seen that this signal arises primarily from the three-body fragmentation of CS_2 through either the (2,1,1) or (2,1,2) channels, with the latter possessing greater momentum due to two $2+$ charge states (Channels 3 and 4). A minor contribution from the (2,0,1) channel (Channel 5) is also visible.

Within Channels 3 and 4 there is a notable change after the first picosecond, with the short-delay transient feature disappearing, and instead the emergence of a Coulomb curve. This curve starts at 200 a.u., and gradually decreases in momentum with increasing delay to 80 a.u.. This curve is attributed to probing a photodissociating CS_2 molecule, where increasing separation of the dissociated fragments leads to increasingly lower Coulombic repulsion. A fainter, less intense feature is visible between 100 and 180 a.u. in Channels 2 and 4, and this is the result of the fragmentation of a multiply charged dissociated CS fragment into S^{2+} and C^+ .

The final feature of note is constant momentum signal at momenta of 80 a.u. and below, that occurs a short delay after t_0 . This feature is also present in the momentum distributions of S^{3+} and S^{4+} (Figures 6.9(b) and (c)). This feature is the result of S^{2+} recoiling against a neutral CS fragment ((2,0,0), Channels 1 and 6). A slightly higher momentum feature also exists for recoil of S^{2+} against neutral S and C where the S^{2+} is produced by probing of the dissociated CS ((0,0,2), Channel 7).

The delayed onset time of this feature is the result of a charge transfer process, by which at short inter-atomic separation charge can migrate from the neutral fragment to stabilise the greater positive charge. The greater delay in onset time with higher charge states is due to a greater critical distance at which charge transfer no longer occurs (as explained in Section 2.5). The signal is absent at short delays as after charge migration two charged fragments exist, and so there is a much greater fragment momenta due to there now being a Coulombic component to their velocities. A variety of different charge transfer processes can occur here, as a result of both the sulfur singlet and triplet products existing, as well as the possibility

Table 6.3: Values of R_{crit} determined using an OTB model for different processes that produce S⁺ and S²⁺.

Pathway	R_{crit} (Å)
S ²⁺ + CS → S ⁺ + CS ⁺	4.86
S ³⁺ + CS → S ²⁺ + CS ⁺	5.67
S(³ P) + CS ²⁺ → S ⁺ + CS ⁺	5.32
S(³ P) + CS ³⁺ → S ²⁺ + CS ⁺	6.20
S(¹ D) + CS ²⁺ → S ⁺ + CS ⁺	4.98
S(¹ D) + CS ³⁺ → S ²⁺ + CS ⁺	5.81

of both two- and three-body fragmentation. Table 6.3 shows OTB predictions for the different possible charge transfer processes that can occur. Due to the vast number of possible channels, only processes which produce S⁺ and S²⁺ are shown, although it can be assumed a similar process occurs for the creation of higher sulfur charge states. Equation 2.8 in Section 2.5 was used to obtain these values, and ionisation potentials of 11.06, 10.36 and 11.33 eV were used for S(¹D), S(³P) and CS respectively[137, 138]. As mentioned in Section 6.3.3, these OTB values for R_{crit} were used to assign a value of R_{crit} for use in generating the simulations.

Prior work has shown that both the singlet and triplet sulfur photoproducts are produced in this photodissociation[136]. It is unfortunately difficult to determine here a precise branching ratio of these products, as there is significant overlap between the velocity distributions of the singlet and triplet channels. There is also overlap with channels that result in ionisation of both the dissociated sulfur and the neutral CS fragment. However, it is still possible to determine which of the two channels is dominant, by looking at the integrated velocity distributions of the low momentum channel from delays of 0 to 0.6 ps (chosen to try and minimise any contribution from the Coulomb curve merging with the low-momentum channel). Shown in Figure 6.26 is a comparison of the velocity distributions of the S²⁺, CS⁺ and CS²⁺ ions (in black), compared to the singlet and triplet velocity data obtained by Brouard and coworkers at 193.3 nm[136]. For all three of these ions broad agreement is seen, and indicates that the triplet channel is dominant, consistent with previous work[139, 140]. The lack of high velocity signal in the CSⁿ⁺ ion distributions also indicates that the high velocity signal (>2500 ms⁻¹) in S²⁺ is

from overlap with multiple ionised fragments, and not part of the dissociation involving neutral cofragments.

6.3.6 C^+ Analysis

Investigation of the time-dependent C^+ ion signal will conclude this Chapter. Similar to the previous two ion analyses, Figure 6.27 shows the experimental and simulated C^+ momentum distributions.

It is apparent that there is again a strong agreement between the experimental and simulated data, lending further support to the accuracy of the parameters and channels chosen to produce it. As expected, a transient feature is visible at short delays between ~ 125 and 200 a.u., although overlap with other features means that unlike in $S^{1/2+}$, the signal is less isolated and is instead observed as an increase in intensity rather than as a distinct feature. From Figure 6.14, it can be seen that the primary contributors to this transient feature are the (2,1,1) and (2,1,2) channels (Channels 3 and 4). The (1,1,0) and (1,1,1) channels (Channels 7 and 10) also add to this transient signal, but as the enhancements are the result of a low probability charge redistribution, their contribution is minor. The transient feature possessing a greater momentum compared to that at later delays and also when probing the ground state is consistent with what would be expected when considering conservation of momentum. It was proven via the (S^+, S^+) covariance that CS_2 adopts a bent geometry after excitation. This results in a greater partitioning of momentum to the C^+ ion as opposed to a Coulomb explosion from a linear geometry.

The features at momenta of ~ 100 and ~ 150 a.u. are assigned to the probing of the dissociated CS fragment. The different momenta of these features corresponds to whether two or three charges are placed on the CS, which subsequently explodes into either (0,1,1) or (0,1,2) fragments, respectively (Channels 8 and 9 for (0,1,1) and Channel 2 for (0,1,2)).

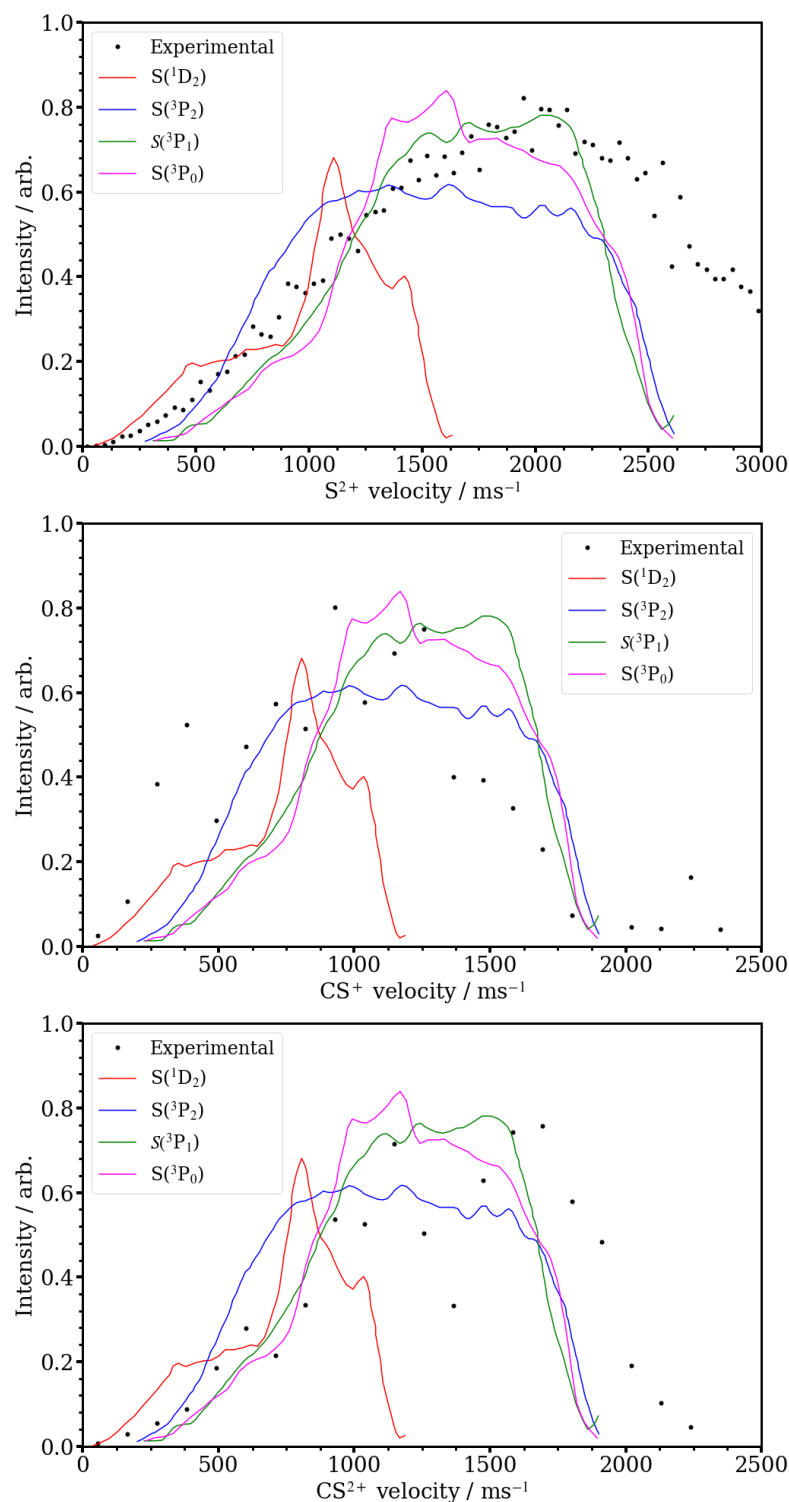


Figure 6.26: Integrated low momentum channel for S^{2+} , CS^+ and CS_2^+ (dotted), compared to corresponding singlet and triplet velocity distributions from Brouard and coworkers (solid)[136]. Conservation of momentum was assumed to obtain the CS^{n+} velocity from S^{2+} velocity. Due to differences in the intensity scale for experimental versus reference data, an arbitrary scale factor was applied to enable comparison.

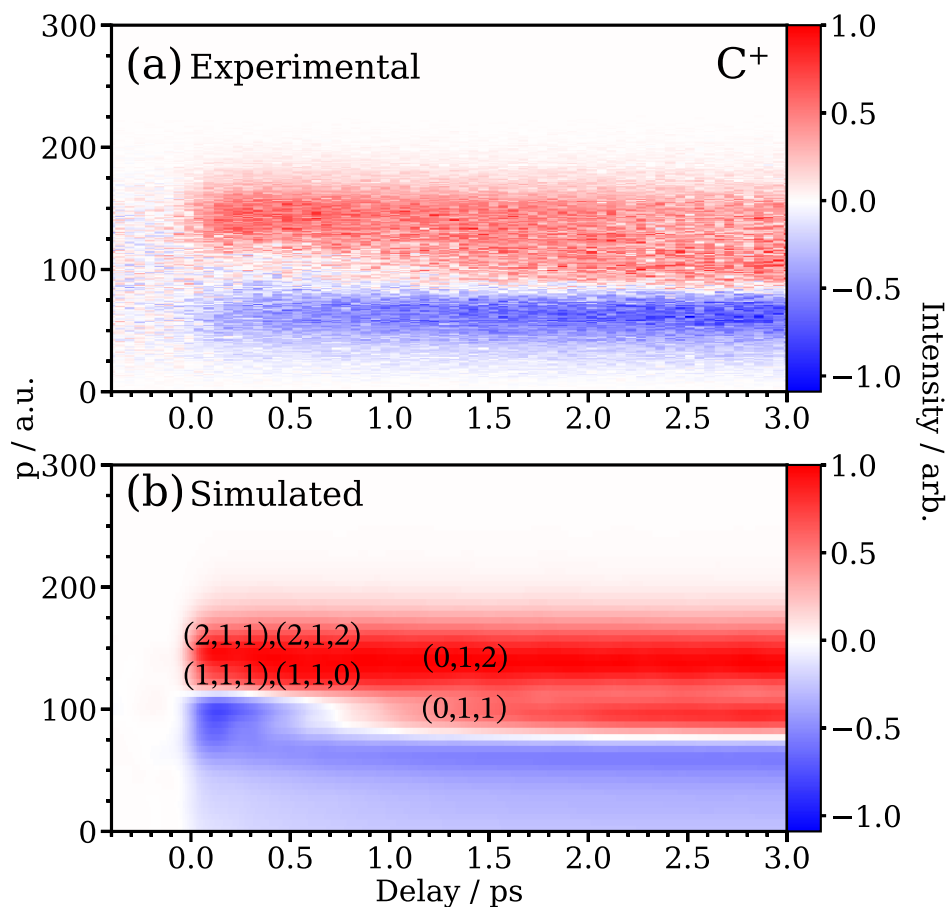


Figure 6.27: Comparison of the experimental subtracted C^+ momentum distribution to the optimised simulated C^+ momentum distribution. Labelled in panel (b) are the simulated reaction channels corresponding to each signal.

6.4 Summary

This Chapter has investigated the ultrafast photodissociation dynamics of CS_2 using a 201.5 nm pump pulse and a 6.9 nm probe pulse, tuned to ionise above the S 2p edge. Analysis focused on the dynamics of S^+ , S^{2+} and C^+ , as from the momentum distributions of the higher charge state ions (in particular $S^{3,4+}$ and C^{2+}), it can be seen that the same features are present in each highly charged ion, and so with the exception of the momenta, the reaction channels are expected to be similar.

Comparison of the experimental momentum distributions to a modelled system, along with time-dependent covariance analysis was able to follow the molecule as it proceeded from a linear ground state, to a bent excited state (with a degree of bending of $135 \pm 40^\circ$), with clear evidence of the bent excited molecule visible

in the subtracted covariance images. The covariance analysis also showed the subsequent dissociation of the excited molecule into S and CS after several hundred femtoseconds, where a late-delay signal for S⁺ recoiling against C⁺ appears. The described model allowed the Coulomb explosion signals that contributed to each time-dependent feature to be determined, with their relative contributions to each feature also being evaluated.

CS₂ has already been the subject of a large quantity of prior investigation using a wide variety of different experimental techniques. As such, the goal of this Chapter was not to further characterise the dissociation of CS₂, rather instead its purpose was to use CS₂ as a benchmark system to demonstrate CEI's capability to follow a molecule through a transient state into the dissociated products. This was accomplished using a combination of the time-dependent momentum distributions and ion-ion covariance analysis, coupled with a simple model of the dissociation. Through this, the Coulomb explosion channels corresponding to each signal in the momentum distribution were identified, and the geometry changes the molecule underwent within the transient state were characterised, in agreement with previous measurements, thus showing CEI's capabilities to identify such properties in future experiments on less studied molecules.

7

Conclusion

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7.1 Summary

The data in this thesis has expanded upon CEI's capability to characterise the photodissociation dynamics of small molecules. Several different studies were presented, conducted at multiple different facilities, with each presenting different properties of a photodissociation that can be measured via CEI. In each case, a ~ 200 nm UV pump pulse was used to excite the molecule, with probe pulses ranging from the soft X-ray to infrared regions used to Coulomb explode it. Velocity-map imaging was used to direct the resultant fragments along a time-of-flight tube, and a variety of detectors and imaging cameras were used to record the fragment arrival coordinates and times. Time-dependent momentum distributions, covariance analysis, and simple modelled systems were used to assign fragments to reaction channels and elucidate the nature of their dynamics.

Chapter 1 provided the motivation for the thesis. Photochemical reactions are relevant to day-to-day life, and possess complicated chemistry due to their ultrafast timescales and significant electronic and structural changes. As such, having as wide a variety of analytical techniques as possible is essential. It was explained that this thesis aims to demonstrate that Coulomb explosion imaging is one such suitable technique, that can complement additional analytical methods.

Chapters 2 and 3 outlined the theory and experimental techniques relevant to the subsequent data chapters. Chapter 2 looked at the effect of different ionisation regimes on the Coulomb explosion, how time-dependent dynamics can be studied by using Coulomb explosion imaging as part of a pump-probe reaction, and gave an overview of photodissociation reactions. Chapter 3 guided the reader through the experimental setup for studying a time-dependent Coulomb explosion experiment. This was accomplished by splitting a CEI experiment into four stages: ion generation, ion direction, ion detection and data processing and analysis. Ion generation dealt with the technical details of the different lasers involved in inducing the Coulomb explosion and initially exciting the molecule. Ion direction introduced the concept of velocity map imaging, the method used to direct any produced ions with the same momentum onto identical points of the detector. Ion detection covered the details of the different detectors and cameras used for collecting the different data sets. Finally data processing and analysis looked at the post-processing applied to the data to decrease noise and convert from radius on the detector to kinetic energy, and then subsequently detailed the two main methods used to interpret the data: converting to 3D momentum distributions, and analysing the covariance between different ions.

Chapter 4 was the first data chapter, and looked at the photodissociation dynamics of CH_2BrI , using data collected at FLASH. Firstly, the time-independent signal, corresponding to FEL-only probing of the ground state molecule, was used to ascertain that for a two-body explosion into a halogen and halomethyl fragment, the charge on the halomethyl is located on the bound halogen rather than the carbon. For a three-body explosion, covariance analysis showed that events where there were both three charged species, and two charged halogens with a neutral methyl occurred.

The time-dependent data was used to determine that at 200 nm, CH_2BrI dissociates via a three-body mechanism by comparison of the fragment internuclear distances to those predicted by a classical over-the-barrier model. As well as identifying that the dissociation was three-body, it was confirmed that the charge transfer process occurs from one halogen to the other, rather than from a carbon to a halogen.

Chapter 5 followed the dissociation dynamics of iodobenzene, collected at the FEL located at SACLA, Japan. Previous theoretical and experimental studies have found that at 200 nm iodobenzene undergoes two independent dissociation mechanisms, leading to either electronic ground-state phenyl and spin-orbit excited iodine or electronically excited phenyl and ground-state iodine photoproducts. Here a global fitting method was applied to characterise the two overlapping constant low-momentum ($p+$, 0) features, corresponding to a charge transfer process. The total translational kinetic energy determined from this global fit was used to identify the amount of energy partitioned into internal modes of the phenyl radical, and this was found to be $44 \pm 10\%$ for the high-momentum channel, and $65 \pm 21\%$ for the low-momentum channel. The optimised basis functions were used to identify a branching ratio of the high-:low-momentum channels of 87:13 with an error of 4%. Rate constants and rise times were evaluated as $0.0084 \pm 0.0004 \text{ s}^{-1}$ and $120 \pm 5.8 \text{ fs}$ for the high-momentum channel, and $0.003 \pm 0.0005 \text{ s}^{-1}$ and $333 \pm 53 \text{ fs}$ for the low-momentum channel, respectively.

A novel use of the charge transfer channel was additionally demonstrated using these channels. The excited state of the cofragment (Ph(X) for the high-momentum channel and Ph(A) for the low-momentum channel) was identified by comparison to an over-the-barrier model, using different ionisation potentials to represent the different cofragment excited states.

Finally, simple modelling of the ($p+$, 1+) Coulomb curves allowed the identity of the cofragment to the dissociation to be confirmed as being a phenyl radical, despite no direct measurement, and this assignment was further supported by additional data collected in a 200 nm UV:800 nm IR laser system, which allowed direct detection of time-dependence in the phenyl radical.

Finally, Chapter 6 studied the photodissociation dynamics of CS_2 , with data again being collected at FLASH. In this study, a modelled system was created, which enabled simulation of the Coulomb explosion dynamics of S^+ , S^{2+} and C^+ after photoexcitation. These ions were chosen as they can account for the vast majority of CS_2 dynamics, with the higher charge state ions possessing similar signals, simply with higher momenta. The combination of the model and time-dependent covariance analysis allowed the makeup of each reaction channel to be determined, and assigned to corresponding signals in each ion momentum distribution.

Time-dependent covariance analysis of the CS_2 ion signals allowed determination of the degree of bending the molecule undergoes during a dissociation, demonstrating Coulomb explosion imaging's capability to follow the ultrafast structural changes of a molecule while on an excited state. The (S^+, S^+) covariance analysis showed clear evidence of CS_2 's excited state bending, where, after interaction with the UV photon, it proceeds from a largely linear ground-state to a bent state with a measured S-C-S bend angle of 135° . This covariance signal at 135° disappears at later delay times as a result of the molecule subsequently dissociating. With increasing delay evidence was also seen in the (S^+, C^+) covariance image of Coulomb explosion of a dissociated CS fragment, confirming the dissociation at CS_2 at 201.5 nm.

In conclusion, presented here are multiple studies, each of which use Coulomb explosion imaging to characterise different properties associated with a photodissociation, including the many-bodied nature of the dissociation, the branching ratios of overlapping dissociation channels, the excited state of a dissociation cofragment and the degree of bending undergone while in a transient excited state. This serves as evidence for CEI's viability as an experimental method to explore the dissociation dynamics during novel experiments on previously unstudied molecules.

7.2 Future Developments

There are multiple ongoing developments that could further advance the field of CEI. Firstly, the advent of attosecond lasers allows the observation of even more increasingly short timescale dynamics.

Secondly, one of the biggest limitations of CEI currently is applying the technique to larger, more complicated molecules, as the greater the number of molecules in a system the greater the number of possible fragmentation pathways, and hence the more difficult it is to isolate which reaction channel each fragment arises from. There are several potential advances that can simplify the study of larger molecules via CEI. Running experiments at higher frequencies (requiring both FELs and imaging cameras that operate at higher frequencies, as well as sufficiently efficient detectors to record the higher count rate) would allow greater statistics to be obtained, and therefore correlations between fragments from the same reaction channel could be more easily determined. In an ideal world, a system would be designed around recording a high number of shots, but within each shot only a single molecule would be exploded. This would permit coincidence imaging to be utilised to accurately determine the precise origin of each fragment. Alternatively, further advancing acquisition techniques to increase the statistics that can be recorded within an experimental runtime would allow the expansion of the covariance mapping method described within this Thesis. With higher statistics covariance mapping can be extended from two-fold to three-fold, allowing the correlations between three ions to be identified, greatly simplifying the determination of the reaction channel of origin. This can then further be expanded to identify correlations greater than three-fold, using the technique of cumulant mapping pioneered by Frasninski[141].

Finally, being able to run CEI experiments with higher energy resolution would enable the experimental data to be compared to high-level theory to identify the specific electronic states fragments reside on. An example of where higher resolution would directly benefit the work in this would be the possibility of isolating the signals from the singlet and triplet sulfur atoms produced in Chapter 6, and thus determine a branching ratio of these two states. Should the ability of CEI to characterise larger systems be achieved, CEI stands to be a very useful tool in the time-dependent experimentalist's toolbox to follow a molecule from the ground state, through a series of excited states, and to the final products, with state-specific resolution.

Appendices



Optimising CS₂ Simulations

To provide an overview of how the optimum input parameters were determined, Figures A.1-A.6 show the effect of varying each simulation parameter on the simulated distributions, as well as showing the optimised simulation compared to the experimental data.

Figure A.1 gives an example of how changing the channel probability affects the summed distributions. This was done here by reducing the probability of the five channels that have a probability greater than 10% by 10% (e.g. from 17.5% to 7.5% for Channel 2), and increasing the probability of the five channels that have a probability of less than 10% by 10% (e.g. from 5% to 15% for Channel 10), hence keeping the total probability at 100%. It can be seen from Fig. A.1(a), while the S²⁺ signal is still largely similar, there are significant differences in both the S⁺ and C⁺ distributions. The transient S⁺ feature has decreased in momentum, and now appears to have merged with the low momentum feature, while the low momentum feature at 80 - 100 a.u. in the C⁺ distribution is now absent.

Figure A.2 gives an example of changing the number of fragmentation channels employed by the simulation. This was done by removing all but the five highest probability channels (1,2,3,5 and 8) from Table 6.2. Notable differences are visible in the S⁺ distribution, with the negative signal at 100 a.u. in S⁺ now extending

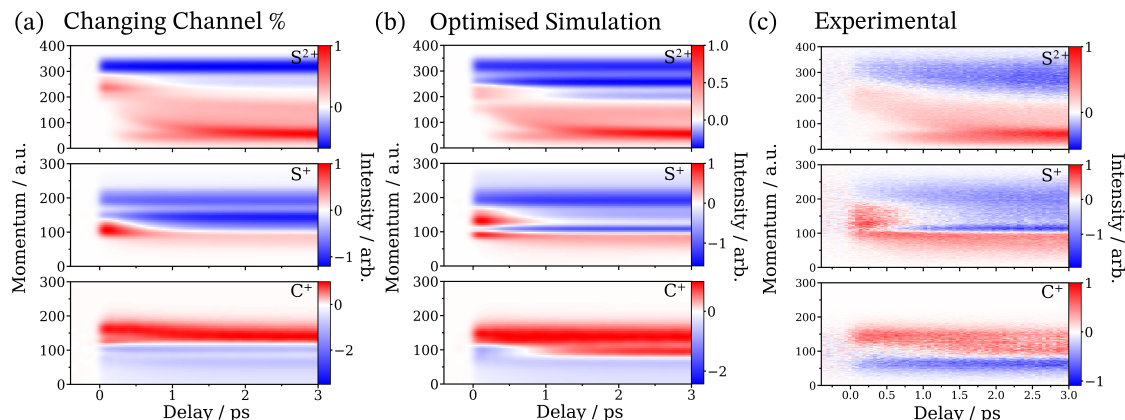


Figure A.1: Panel (a) shows the effect of changing the probability of each simulated reaction channel. Of the channels listed in Table 1, channels 4,6,7,9 and 10 had their probability increased by 10 %, and channels 1,2,3,5 and 8 were decreased by 10%. Panels (b) and (c) show the optimised simulation and experimental data for comparison.

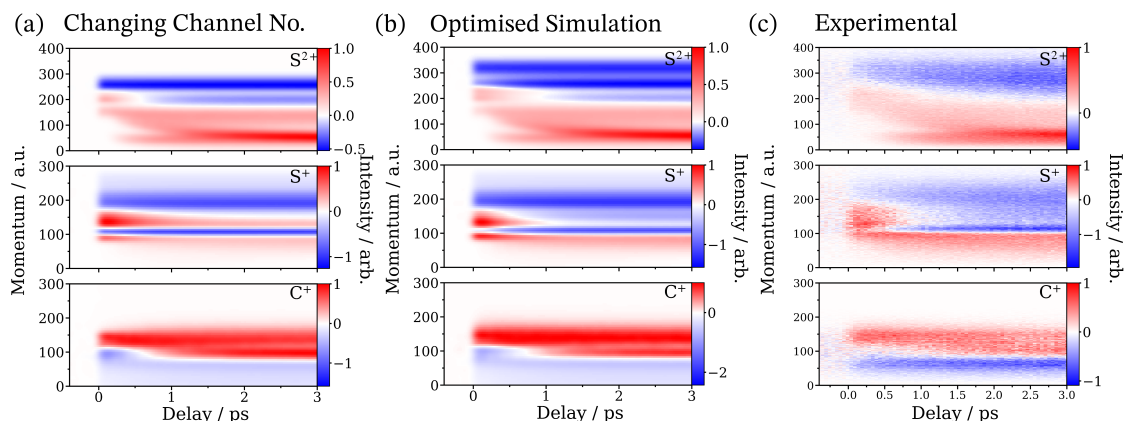


Figure A.2: Panel (a) shows the effect of decreasing the total number of channels in the simulation. This simulation only uses the five highest probability channels in Table 1 (1,2,3,5 and 8). Panels (b) and (c) show the optimised simulation and experimental data for comparison.

to a shorter delay range, and a constant momentum channel is also present at ~ 140 a.u. from 0.7 - 3 ps.

Figure A.3 gives an example of changing the charge distribution within the molecule. There were many different ways to accomplish this, but here is shown the effect of swapping the charge on two ions in each channel. For channels where the sulfur ions have non-equivalent charges, the charges on those two sulfur ions were swapped. In channels where the two sulfurs had equivalent charges, the charge on the two ions resulting from the fragmentation of the CS product were swapped, so as to ensure each channel always had a change in charge distribution. This has a

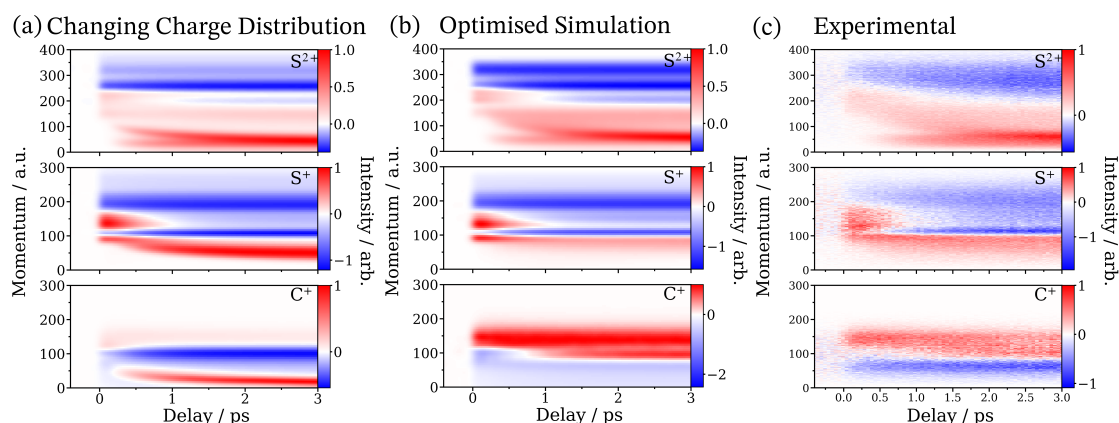


Figure A.3: Panel (a) shows the effect of changing the charge distribution within each channel. For each channel the total charge was kept constant, but the charge applied to each atom varied. Panels (b) and (c) show the optimised simulation and experimental data for comparison.

significant effect on both the S^+ and C^+ distributions, with a broadening of the low momentum feature in S^+ and a complete changing of the C^+ distribution.

Figure A.4 gives an example of changing the degree of bending within the molecule for each of the ground and excited states. For each of the states both the angle and standard deviation were adjusted arbitrarily by 20% in both directions. When the angles are decreased, the momentum of the transient feature in S^+ and S^{2+} decreases, and new depletions are visible in the C^+ distribution. Different changes are seen when the angle is increased by 20%, most notably in the C^+ distribution, with the low momentum channel greatly increasing intensity compared the high momentum channel. The spread of this high momentum channel also increases.

Similar to Figure A.4, Figure A.5 adjusts each bond length in each state by 20% in both directions. This produces smaller changes to some of the other adjustments shown, with simply a slight variation in momentum of all features. Decreasing length increases the momenta of the features (due to greater Coulombic repulsion), while increasing lengths causes a decrease in momenta (due to lesser Coulombic repulsion).

The final parameter that was optimised was R_{crit} , shown in Figure A.6. Rather than adjusting the critical distance by a percentage, here it was shifted to two extreme values, 2 Å and 10 Å, to account for values just longer than the bond lengths, and far greater than the bond lengths. The main effect this has on the

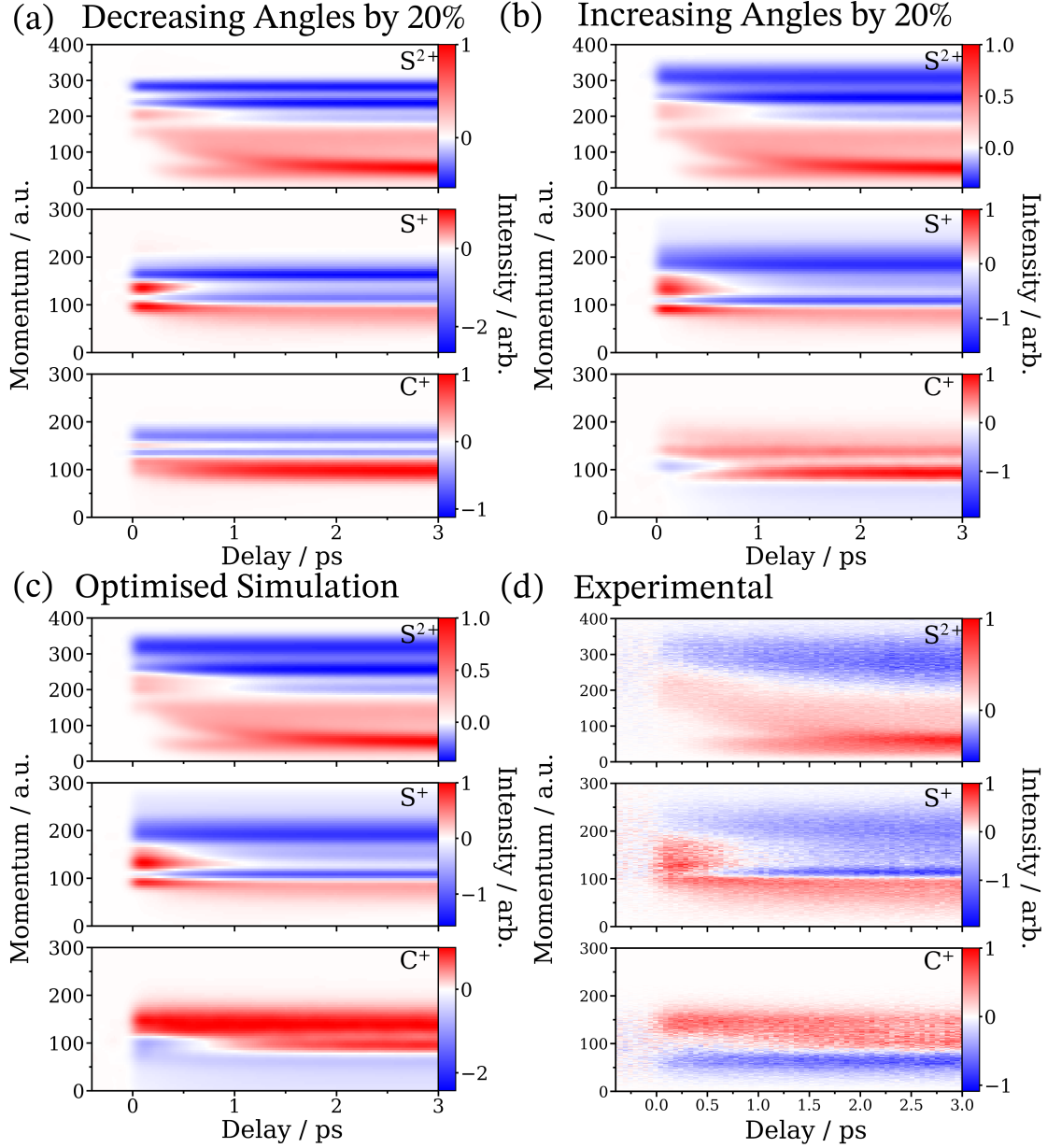


Figure A.4: Panels (a) and (b) show the effect of adjusting the degree of bending in the different states. For each state the angle and standard deviations were decreased and increased by 20%, respectively. Panels (c) and (d) show the optimised simulation and experimental data for comparison.

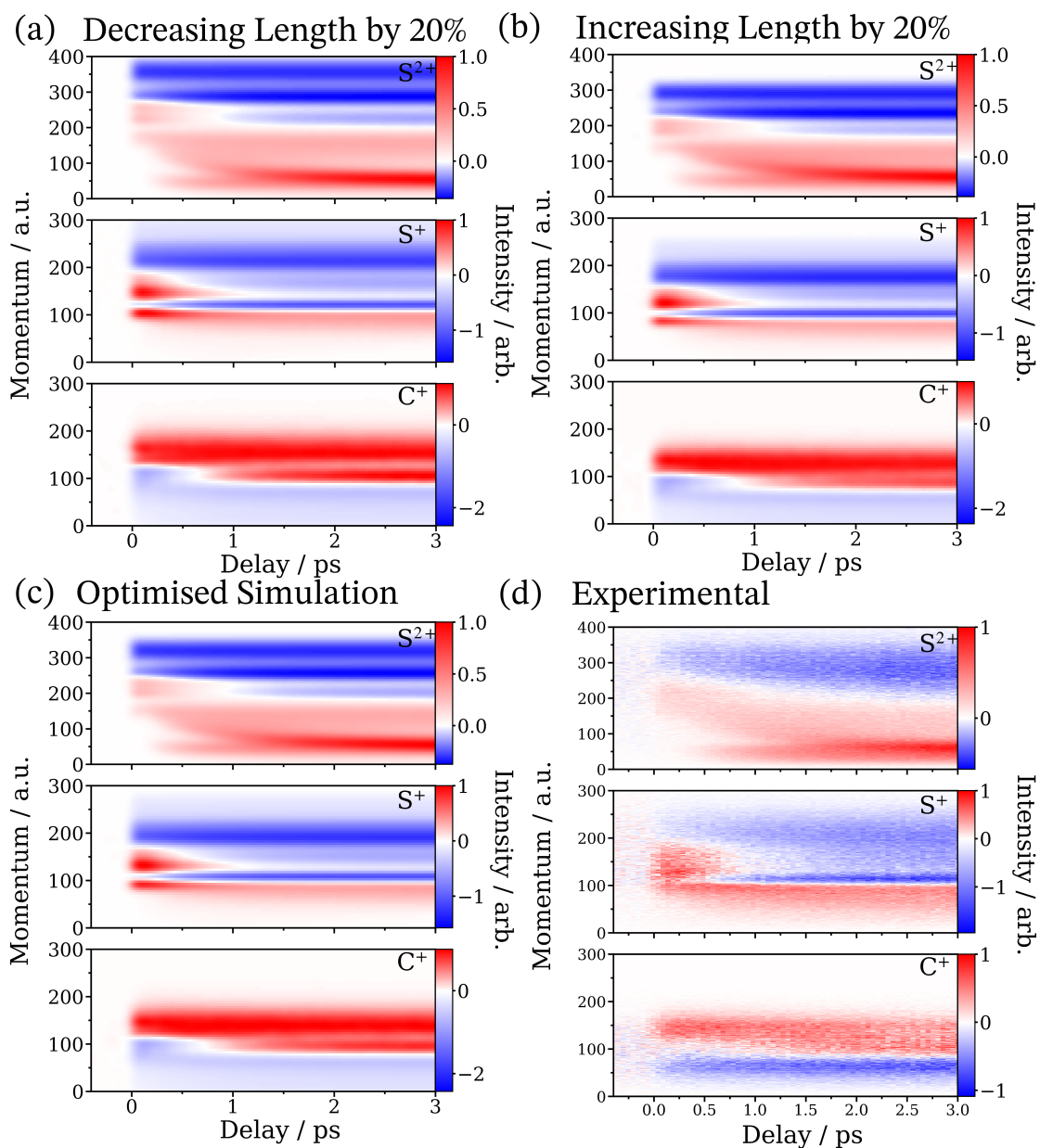


Figure A.5: Panels (a) and (b) show the effect of adjusting the bond length in the different states. For each state the bond lengths and standard deviations were decreased and increased by 20%, respectively. Panels (c) and (d) show the optimised simulation and experimental data for comparison.

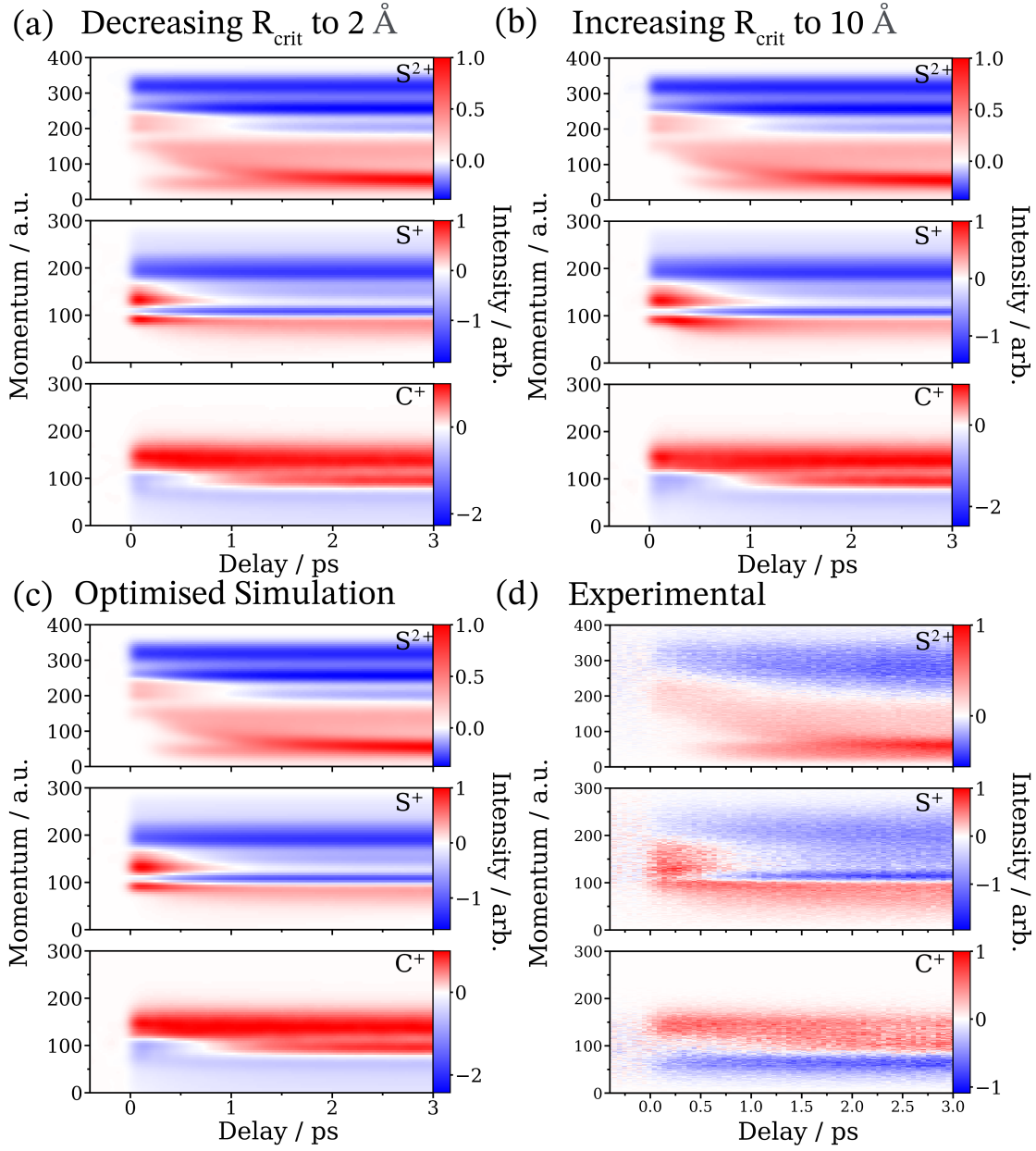


Figure A.6: Panels (a) and (b) show the effect of changing the critical distance value used. This value was decreased to 2.0 Å and increased to 10 Å, respectively. Panels (c) and (d) show the optimised simulation and experimental data for comparison.

distributions is in the onset time of the low momentum feature in S^{2+} , with it occurring essentially concurrently with the pulse overlap at 2 Å, whereas it exists at longer timescales at 10 Å. The optimised simulation parameters were used along with covariance analysis to interpret the experimental signals in Chapter 6.

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