

Time-resolved Studies of Photoinduced Dynamics using Fast Imaging Sensors



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A thesis submitted for the degree of Doctor of Philosophy
Physical and Theoretical Chemistry

Michaelmas 2020

Acknowledgements

First and foremost, I would like to thank my supervisor, Professor Mark Brouard. Without his endless support, encouragement, and patience this would not have been possible. Friday evening refreshments, in those halcyon days, were a constant source of revitalisation and inspiration for my work.

I would also like to thank the brilliant Dr Rebecca Boll and Professor Daniel Rolles for countless invaluable meetings and frantic email discussions. Their leadership and enthusiasm during difficult beamtimes at FLASH was unparalleled. I am also indebted to Felix Allum for his excellent advice throughout and without whom I would probably to this day still be searching for evasive computer files. No question has ever been too big or small and I am grateful for all the guidance you have given me. I would also like to thank Dr Robert Burleigh for his support throughout his time in the group and at Jesus college and who definitely ensured that no day was uneventful. I've also been inspired by Dr Ruairidh Forbes for his unrelenting enthusiasm for science even at the end of a fourteen hour night shift albeit with a weissbier to wash things down. The entire Brouard group, past and present, have helped me in one way or another and I would like to thank each of you. Tea breaks were always an unpredictable affair, grappling with some of life's most tantalising questions. I'd also like to thank all members of the Brouard run club especially our leader, Dr Cornelia Heid, who encouraged me that I really did want to go even when I thought otherwise.

I would like to express my gratitude to the exceptional teams of the mechanical and electronic workshops. Your (many) competent and calm interventions have been crucial to much of the work done in Oxford. Andy, Steve, John, Phil, and Robert deserve particular thanks for their enthusiasm, willingness, and problem solving when all seemed lost.

I would also like to thank my friends and family for their unswerving support and faith over the years. To Lily and Fen, I don't know what I would do without either of you. Thank you Ally Leitch for helping me to take my mind off things all too easily. Special thanks must also go to Professor Chris Butler and family for their continuous support and to Lee and Jacey for helping to create such a comfortable home space. I'd particularly like to thank my parents for always supporting and believing in me.

Lastly, I need to thank Sophie. I wish that you could be with me on this day. Nothing would have been possible without you and I am grateful for your

never-ending belief in me and world-reaching support for me. Thank you for being a constant source of inspiration to me, I know I couldn't be here without you by my side. This one's for you.

Abstract

In this thesis, the three-dimensional, multi-mass, and covariance imaging capabilities of the Pixel Imaging Mass Spectrometry (PIImMS) camera has been demonstrated in a range of velocity-map imaging (VMI) experiments.

The development of an experimental configuration for VMI experiments allows for three-dimensional imaging with high velocity resolution along the time-of-flight axis. This was demonstrated by recording the full three-dimensional velocity distributions of CO and S photofragments, following the photodissociation of OCS, with the PIImMS camera. The resultant velocity distributions are sufficiently well resolved to express as an expansion of spherical harmonics. This was further emphasised through the investigation of a system with no axis of cylindrical symmetry and therefore unsuitable for simple conventional VMI experiments.

The ultraviolet (UV) photoexcitation dynamics ($\lambda = 267$ nm) of 2(5H)-thiophenone were studied by ultrafast time-resolved Coulomb explosion imaging. The Coulomb explosion of the system was probed separately *via* strong-field and inner-shell ionisation. The velocity-dependent ion channels arising from an intense non-resonant infrared (IR) ($\lambda = 801$ nm) probe provide information on the photoexcitation dynamics of thiophenone. The channels derived from Coulomb explosions are supported through covariance analysis. The photoexcitation scheme and delay-dependent covariance analysis are tentatively attributed to a prompt ring-opening of thiophenone, within 300 fs. The UV photoexcitation of thiophenone probed *via* XUV ionisation revealed many ion correlations were revealed through time-of-flight covariance analysis, supported by angular covariance. The velocity-dependent ion yields are notably different to the UV-IR which is unsurprising given the nature of ionisation.

Coulomb explosion imaging experiments of OCS were performed induced by an intense IR pulse at varying laser intensities. The rich and complicated Coulomb explosion dynamics were determined through various covariance analyses. Through these analyses, minor channels and branching ratios were identified.

Contents

1	Introduction	13
1.1	Photochemistry	13
1.1.1	Photoinduced Molecular Dynamics	15
1.2	Lasers	19
1.2.1	Femtochemistry	20
1.3	Ion Imaging	21
1.3.1	Velocity Map Imaging	22
1.3.2	Multi-mass Imaging	23
1.4	Photoproduct Correlation	26
1.4.1	Coincidence Imaging	27
1.4.2	Covariance Imaging	28
1.4.3	Diffraction Imaging	29
1.5	Outline of Thesis	29
2	Experimental Principles and Apparatus	31
2.1	Experimental Principles	31
2.2	The Oxford VMI Spectrometer	32
2.2.1	Overview	32
2.2.2	Ion Optics	34
2.2.3	Detector	35
2.2.4	Optical Systems	36
2.3	The FLASH VMI Spectrometer	39
2.3.1	Overview	39
2.3.2	Ion Optics	41

2.3.3	Detector	42
2.3.4	Optical Systems	42
2.3.5	Free-electron lasers	43
2.4	FLASH Diagnostic System	45
2.4.1	Gas Monitor Detection	47
2.4.2	Bunch Arrival Monitor	47
2.4.3	Streak Camera	48
2.4.4	Illustrative Example	49
2.5	The PImMS Camera	52
2.5.1	Cluster Analysis	54
2.5.2	Image Analysis	56
2.6	Summary	58
3	Post Extraction Inversion Slice Imaging	59
3.1	VMI Techniques	59
3.2	Post Extraction Inversion Slice Imaging	62
3.2.1	Concept	63
3.2.2	Ion Optic Configuration	68
3.3	Simulations	71
3.3.1	3D slice images	71
3.3.2	Time-of-Flight Profile	73
3.4	Experimental Methods	79
3.5	Experimental Results	80
3.5.1	Quantitative Measures	81
3.5.2	High Extraction Field	83
3.5.3	Low extraction field	88
3.5.4	Detection Efficiency of Ionic Photofragments	94
3.5.5	Multiple Ion Extraction	101
3.6	Future Work and Conclusions	109

4 Spherical Harmonic Expansion Projection of Experimental Ion Images	111
4.1 Introduction	111
4.1.1 Photofragment Spatial Distribution Extraction	112
4.2 Experimental Results	113
4.2.1 Data Manipulation	114
4.2.2 Low Rotational State CO Photofragments	115
4.2.3 High Rotational State CO Photofragments	118
4.3 System with a rotated axis of polarisation	120
4.3.1 Experimental Methods	121
4.3.2 Experimental Results	123
4.4 Conclusion	131
4.5 Future Work	133
5 Principles of Coulomb Explosion Imaging	135
5.1 Background	135
5.2 Intense Laser Field Ionisation	138
5.3 Inner-Shell Ionisation	139
5.3.1 Relaxation Processes	141
5.3.2 XUV Lightsources	143
5.4 Covariance Analysis	145
5.4.1 Time-of-Flight Covariance	145
5.4.2 Recoil-Frame Angular Covariance	149
5.4.3 Radial Covariance	151
5.5 Summary	152
6 The Photochemistry of Thiophenone: 1	153
6.1 Introduction and Background	153
6.2 Experimental Methods	156
6.2.1 Overview	156
6.3 Experimental Results: Pump and Probe Dynamics	157

6.3.1	UV Pump Induced Dynamics	157
6.3.2	IR Probe Pulse Dynamics	161
6.4	Experimental Results: Pump-Probe Excitation Dynamics	164
6.4.1	Time-of-Flight Analysis	165
6.4.2	Velocity-dependent Channels	166
6.4.3	Discussion	174
6.5	Ion correlations through Covariance Analysis	176
6.5.1	Delay-dependent Covariance	180
6.5.2	Discussion	184
6.6	High UV Intensity Dynamics	186
6.7	Conclusions	187
7	The Photochemistry of Thiophenone: 2	189
7.1	Introduction	189
7.2	Experimental Overview	189
7.2.1	Experimental Set-up	190
7.2.2	Data Correction	190
7.3	Experimental Results: FEL Only	190
7.3.1	Time-of-Flight Analysis	190
7.3.2	Time-of-Flight Covariance	191
7.3.3	Angular Covariance	194
7.4	Pump-probe Dynamics	196
7.4.1	Time-of-Flight Analysis	196
7.4.2	Ion Image Analysis	198
7.4.3	Time-of-Flight Covariance	206
7.4.4	Angular Covariance	213
7.4.5	Delay-dependent Covariance	218
7.4.6	Discussion	221
7.5	Conclusion	222
7.5.1	Future Experiments	222

8 Strong-Field Ionisation Dynamics of OCS	225
8.1 Introduction	225
8.2 Experimental Methods	225
8.3 Coulomb Explosion Dynamics at Low Intensity	226
8.3.1 Time-of-Flight Analysis	226
8.3.2 VMI Images	227
8.3.3 Coulomb Explosion Dynamics	229
8.3.3.1	233
8.4 Coulomb Explosion Dynamics at Medium Intensity	236
8.4.1 Time-of-Flight Analysis	236
8.4.2 Coulomb Explosion Dynamics	237
8.5 Coulomb Explosion Dynamics at High pulse energy	241
8.5.1 Time-of-Flight Analysis	241
8.5.2 Coulomb Explosion Dynamics	242
8.6 Abel Inverted Covariance	245
8.7 Radial-radial Covariance	246
8.8 Angle-angle Covariance	248
8.9 Carbon Ions	249
8.10 Discussion	250
8.11 Conclusion	251
9 Conclusions and Future Work	253
9.1 Summary	253
9.2 Future Directions	257
References	261
Appendices	
A Appendix 1	279

1

Introduction

1.1 Photochemistry

The field of photochemistry concerns chemical changes through interaction of matter with light. This subset of chemistry is fundamental to the understanding of a myriad of processes. Many of these processes form the basis for some of the most rudimentary necessities for life on Earth. The most notable and well-known of these is perhaps photosynthesis; the process used by plants and other organisms that converts carbon dioxide into chemical energy (in the form of sugars) is driven by the absorption of sunlight[1]. Significant photochemical processes occur constantly in the troposphere and stratosphere of the Earth's atmosphere. These have extensive consequences on the climate and habitability of the planet. In the stratosphere, the ozone-oxygen cycle is the process that reproduces ozone, O_3 , from molecular oxygen, O_2 , by converting ultraviolet (UV) light from the sun into thermal energy[2]. This cycle absorbs all of the most biologically harmful UV light, UV-C ($\lambda < 280$ nm) preventing this radiation from reaching the Earth's surface. Ozone is also very effective at screening UV-B radiation ($\lambda = 315 - 280$ nm) that can cause sunburn and skin cancer in humans. Competing atmospheric photochemical processes result in the permanent removal of ozone from the stratosphere. This has damaging implications on life on Earth through the increase of UV light reaching its surface.

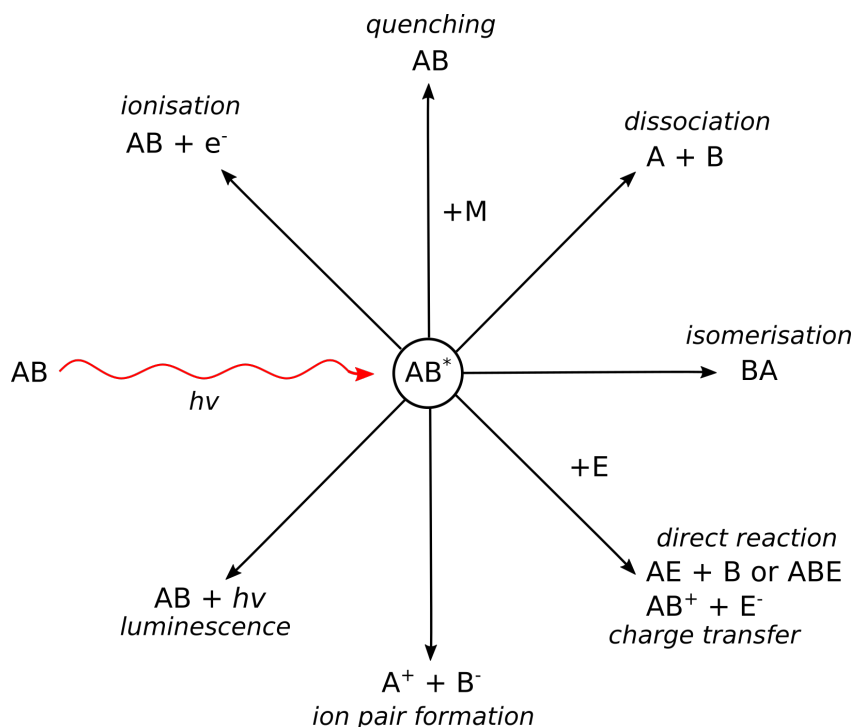


Figure 1.1: Examples of some possible routes of relaxation of an excited molecule AB^* following absorption of a photon.

Photochemistry has also greatly impacted technological advancements in a wide-range of fields. Notable examples include electrical energy generation through solar cell technology, artificial photosynthesis, more efficient industrial reactions through photocatalysis, and organic synthesis[3, 4].

The term photochemistry is an umbrella term that encompasses a wide range of photoexcitations. The quantum nature of atoms and molecules gives rise to complex discrete internal energy levels determined by its nuclear, electronic, vibrational, and rotational characteristics. The absorption of light can promote the atom or molecule from (typically) the ground state to an electronically excited state. From this state, the system may evolve depending on the excited state and relax back to a ground electronic state in a number of ways[5], some of which are outlined in Figure 1.1.

1.1.1 Photoinduced Molecular Dynamics

The properties of a system can be studied through the framework of quantum mechanics by solving the time-independent (or time-dependent) Schrödinger Equation:

$$\mathcal{H}\Psi(r, R) = E\Psi(r, R) \quad (1.1)$$

where $\mathcal{H}$ is the Hamiltonian operator, Ψ is the wave function of the system, E are eigenvalues of the system, and r and R denote all the electronic nuclear coordinates, respectively. The solution of Equation (1.1) leads to the construction of potential energy of the system for all possible combinations of electronic and nuclear coordinates. The Schrödinger Equation can only be solved exactly for the hydrogen (or a hydrogen-like) atom. To solve the Schrödinger Equation for polyelectronic atoms or molecules, approximations must be made to account for the electron-electron interactions. Typical methods include the Hartree-Fock method[6] and the orbital approximation[6]. The most commonly applicable approximation for molecules is the Born-Oppenheimer approximation[7] (BOA). The BOA assumes that the motion of nuclei and electrons may be treated separately, as the nuclei are much heavier than the electrons. The Schrödinger Equation can thus be solved for the electrons at a series of fixed nuclear coordinates, for instance intramolecular bond lengths or angles, in order to construct an approximate potential energy surface (PES) for the system[8]. The nuclear motion can be further simplified into ro-vibrational parts to approximate quantum states of these motions.

$$\Psi_{\text{tot}} \approx \Psi_{\text{el}}(q_{\text{el}})\Psi_{\text{nuc}}(q_{\text{nuc}}) \quad (1.2)$$

$$\Psi_{\text{tot}} \approx \Psi_{\text{el}}(q_{\text{el}})\Psi_{\text{vib}}(q_{\text{vib}})\Psi_{\text{rot}}(q_{\text{rot}}) \quad (1.3)$$

$$E_{\text{tot}} = E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}} \quad (1.4)$$

where E_i are the energies of each motion and q_i are the respective coordinates.

The dynamics of a molecule in a specific state, and therefore its ultimate fate (see Figure 1.1), can be fully determined from the shape of the corresponding PES. Attractive surfaces relate to states where there is at least one strongly

bound vibrational state. Repulsive surfaces do not have such a minimum and will result in dissociation.

Despite forming the foundations for much of our understanding of chemical bonding, breakdowns and exceptions to the BOA are pervasive throughout chemistry[9], especially in the context of excited electronic states[10]. Such processes are termed electronically nonadiabatic. In nonadiabatic processes, nuclei move on more than one potential energy surface and occur when two or more PESs lie close in energy. Of particular significance are ‘conical intersections’: the position where two PESs cross and ultrafast radiationless surface crossing can occur[9–11]. These lead to unexpected photodynamics that can be observed spectroscopically. The time-dependent Schrödinger equation is relevant to the evolution of photoproducts on these surfaces as it describes the state of the system as a function of time.

This thesis is concerned with the investigations of photodynamical processes that ultimately result in the production of positively charged ions following some induced photochemistry of ground state molecules. The photodynamical processes that will be studied are molecular dissociations, including Coulomb explosions, and isomerisations.

Photodissociation

Photodissociation refers to the breaking of a chemical bond after absorption of one or more photons and the formation of two fragments. Photodissociation is a broad term for the variety of means by which a molecule can ultimately dissociate. However, all photodissociations are founded with an electronic excitation.

The manner of photodissociation depends on the topologies of the PES that is associated with the excited state and those of close-lying excited states. Some of these photodissociations are shown in Figure 1.2. Panels (a) and (b) show direct photodissociations *i.e.* the dissociation follows immediately after the photon absorption. In Panel (a), a molecule AB is excited to a bound excited state, however the nuclear geometry of A and B corresponds to an unbound state and is therefore dissociated. In Panel (b), the molecule is excited onto a repulsive state which

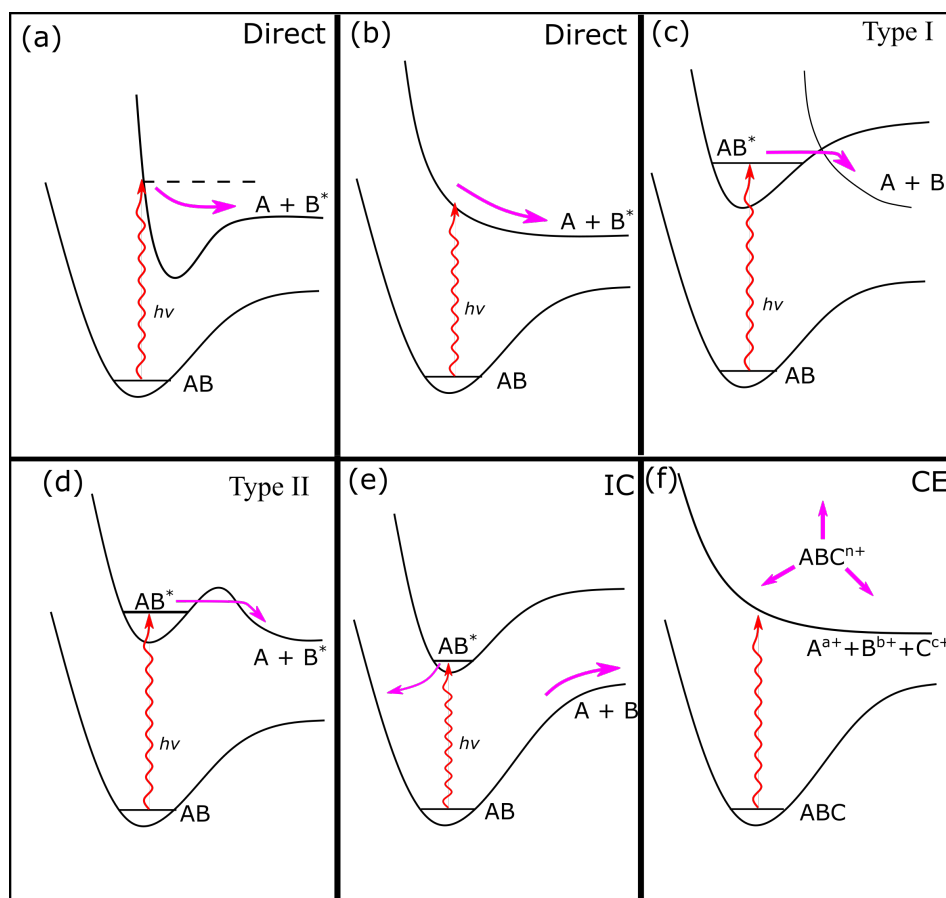
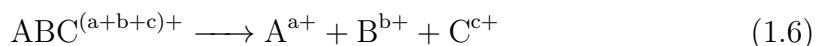
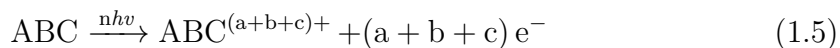


Figure 1.2: Examples of some possible photodissociations following electronic excitation *via* photon absorption. (a) direct photodissociation *via* a bound excited state; (b) direct photodissociation *via* a repulsive excited state; (c) Herzberg type I or electronic predissociation, molecule undergoes a transition from a bound excited state to a repulsive excited state; (d) Herzberg Type II, molecule is excited to a quasi-bound excited state which can be overcome through IVR or tunnelling through the barrier; (e) dissociation following non-radiative internal conversion onto the ground electronically excited state in a highly excited vibrational (or rotational) state; (f) Photon-induced Coulomb explosion following rapid removal of multiple core electrons.

results in dissociation. Panels (c) and (d) correspond to Herzberg Types I and II dissociations, respectively. In Panel (c), the molecule undergoes a transition *via* a conical intersection from a bound excited electronic state onto a repulsive excited state. In Panel (d), the molecule is excited onto a quasi-bound state which can be overcome through tunnelling or intramolecular vibrational-energy redistribution (IVR). In Panel (e), the molecule is excited to AB^* and undergoes radiationless internal conversion (IC) onto the ground electronically excited state in a highly excited vibrational or rotational state. The molecule then undergoes dissociation[12].

Panel (f) shows a molecule ABC undergoing a light-induced Coulomb explosion. A Coulomb explosion is a special class of dissociation whereby multiple electrons are initially rapidly removed resulting in a highly charged, unstable polycation. The strong intramolecular Coulomb repulsion subsequently causes a rapid dissociation[13]. The removal of many electrons effectively reduces the chemical bonding of the molecule and consequently the final velocities of photofragment ions are chiefly determined by the classical electrostatic potential associated with the internuclear separation of fragment ions, immediately after ionisation. A Coulomb explosion photodissociation can be generalised:



The ejected electrons will not be included in such photodissociation equations hereafter.

There are a number of methods of removing electrons to induce a Coulomb explosion in a target molecule such as strong-field ionisation, inner-shell ionisation, and collision of high energy molecules with a thin foil. Coulomb explosions and the associated dynamics are the subject of investigations in the latter half of this thesis and Chapter 5 will discuss the principles of Coulomb explosions in much greater detail.

By studying the dynamics of photodissociations in terms of the quantum state populations, velocity distributions, direction of recoil, and angular momentum polarisation of the photoproducts, a clearer understanding can be obtained of the topology and contribution of the PES(s) involved[12, 14, 15].

Photoisomerisation

Photoisomerisation is the photoinduced isomerisation of a molecule whereby a bond is broken or rotated to change the original structure. This could be a photochemical interconversion of *cis-trans* isomers[16] or permanent ring-opening processes[17, 18]. Photoisomerisations occur *via* one or more excited electronic states before relaxation

to the ground state of a structural isomer. The nature and exact mechanism of these isomerisations are varied and highly specific to individual systems which render such photochemical reactions very difficult to study, especially in the gas-phase[14].

The *cis-trans* isomerisation of ethene can occur *via* absorption of light. The lowest excited singlet and triplet states of ethene are (π, π^*) . Following absorption of a photon, the change in electronic configuration loosens the restriction that holds the molecule in a planar geometry and rotation about the carbon-carbon axis becomes possible. Subsequent relaxation to the ground state *via* a conical intersection reimposes a planar geometry on the molecule, however there is no preference of isomer and both *cis*- and *trans*- isomers are formed[5].

1.2 Lasers

The ability to investigate the photochemistry of systems was greatly advanced by the development of laser technology[19, 20]. A key characteristic of laser light is its monochromaticity and hence very well-defined photon energies. This allowed photochemists to prepare atoms or molecules in distinct excited states and study the photodynamics therein. Furthermore, laser light is coherent, highly directional, and capable of being produced in short pulses resulting in unprecedented laboratory light intensities that could be intersected with a molecular beam of target molecules and fragments detected by ion time-of-flight. This allowed the photodissociation and photofragmentation of systems to be studied gleaned fragmentation dynamics, relative fragmentation yields, and kinetic energy releases of the fragments. Wavelength tunability also significantly increased the scope of systems that could be investigated[21].

A powerful extension to these laser experiments is the concept of ‘pump-probe’ experiments. These employ a combination of two laser pulses to firstly initiate some photochemistry of a system with a ‘pump’ laser pulse and later probe the system with the second pulse of light. The ‘probe’ pulse induces an observable photochemical process in the system, such as resonance-enhanced multiphoton ionisation[22, 23] or laser-induced fluorescence[24]. The time-delay between laser

pulses can be precisely chosen to probe the system in a time-resolved manner. This allows the system to evolve temporally on the prepared excited state and time-resolved information of the photochemical process can be retrieved. Alternatively, the choice of wavelength or laser polarisation of the pump and probe pulses can be changed to observe which photoproducts are affected and the distribution of these photoproducts. Both of these provide information on the nature of the accessible excited state(s)[15, 25] and associated symmetry.

1.2.1 Femtochemistry

Physical molecular processes such as molecular break-up, isomerisations, and vibrational motion occur on the order of tens of femtoseconds (10^{-15} s). In order to investigate these dynamics, measurements must also be made on these timescales, an unattainable ambition until the 1980s. The advent of ultrashort (< 100 fs) light sources heralded a new era to the study of chemical dynamics[26, 27] through the possibility of time-resolved measurements on such timescales. Ultrafast time-resolved pump-probe studies allow for an evolving system to be probed as the reaction unfolds. The probe pulse initiates an observable quantity in the system that can be recorded at varying pump-probe delays to build up ‘snapshots’ of the reaction as the wavepacket traverses the excited state.

Such ultrafast pump-probe experiments were first performed by Ahmed Zewail[28], who would later be awarded the Nobel Prize in Chemistry for his pioneering work in the emergence of the field of femtochemistry[29, 30]. In one of these experiments, the photodissociation of iodine cyanide, ICN, was studied. ICN molecules were excited from its ground electronic state to a repulsive state by a femtosecond pulse ($\lambda = 307$ nm) and subsequently probed by a second femtosecond pulse ($\lambda = 388.5$ nm). The delayed rise in fluorescence signal of free CN fragments inferred the existence of the long-predicted short-lived transition states, in this case ICN*[31]. The real-time dynamics of intramolecular hydrogen atom-transfer processes under collisionless conditions were also studied using femtosecond depletion techniques[32]. The motion of the hydrogen atom transfer was observed to take

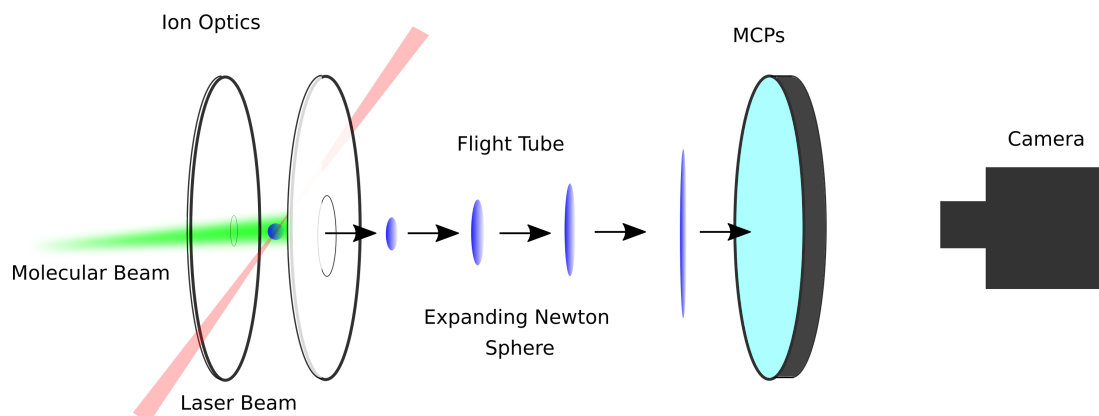


Figure 1.3: Schematic of an ion imaging experiment showing the key components. The expanding Newton sphere of ions is shown at various times before arriving at the detector.

place within 60 fs. In experiments on NaI[33–35], a femtosecond pump pulse was used to excite the molecule to a coherent superposition of excited vibrational states. The excited molecules are then trapped in a potential well where they oscillate with a fixed period. At the end of each of these oscillations within the well, the wave packet may undergo a non-adiabatic curve-crossing to the covalent surface with products Na and I.

This emerging field has paved the way for the real-time studies of a range of previously impossible photodynamical experiments, including photodissociation[36–41], and nonadiabatic systems such as charge transfer[42].

1.3 Ion Imaging

The advancements in laser capabilities allowed for a wide-range of photochemical processes to be accessed. Further, a number of detection techniques provided the means to probe the systems. Typically time-of-flight mass spectrometry (ToF-MS) and laser induced fluorescence techniques were employed. The invention of single-particle imaging by Chandler and Houston[43] in 1987 allowed concurrent developments in spectroscopic techniques. The technique of ion imaging provided measurements for the kinetic energy and angular distributions of photoproducts. Since its inception, ion imaging quickly became an indispensable tool for experimentalists across a spectrum of fields.

In ion imaging, a sample gas is supersonically expanded into the experimental chamber at high vacuum (1×10^{-7} mbar) through a pulse valve and is collimated by at least one skimmer to form a rotationally cold molecular beam. The molecular beam is then intersected by one or more focussed laser pulses to induce some photochemistry and ionise the photoproducts. The nascent ions are then accelerated by an electric field onto a two-dimensional position-sensitive detector. The Newton sphere of ions expands orthogonally to the time-of-flight axis. The detectors typically comprise a dual stack of microchannel plates (MCPs) coupled to phosphor screen and a camera. When ions or electrons impinge on the MCPs a cascade of electrons is produced which are accelerated by a large potential difference across the MCPs onto the phosphor screen. The arriving electrons cause the phosphor screen to emit a localised flash of light which is typically imaged by a CCD camera and thus the time and position of the ion event is recorded. The technique and key components are illustrated schematically in Figure 1.3.

A further consequence of accelerating ions through an electric field is that the time-of-flight is proportional to the square root of the mass-to-charge ratio, m/z , and therefore ions with non-degenerate mass-to-charge ratios are separated temporally at the detector. This can infer useful information on the chemical identity and branching ratios of ions. The energy resolution (10 – 15%) in the original ion imaging experiments was limited by the size of the ionisation region where the molecular beam overlapped with the focussed laser beam resulting in substantial blurring of the ion images. Chandler and Houston also employed grids in order to create homogeneous electric fields. However, grids introduce some disadvantages such as loss of transmission and distortion of ion trajectories.

1.3.1 Velocity Map Imaging

The method of ion imaging was greatly improved with the advent of velocity map imaging (VMI) introduced by Eppink and Parker[44]. Eppink and Parker used two charged electrostatic plates and a grounded electrode, with no grids, in the ion optic set-up. Eppink and Parker employed open electrodes to allow for 100%

transmission of ions to reach the detector. This series of plates act as electrostatic lenses and maps ions, of a given charge q , with an equal transverse velocity onto the same position at the detector, regardless of the position in the interaction region that an ion was formed. This removed blurring to the ion images and led to a significant increase in energy resolution ($2 - 5\%$). In principle, the full three-dimensional velocity distribution can be recorded directly from the velocity mapped image; though in practice other methods or techniques are employed to extract the velocity and angular distributions.

The radial distribution of a velocity mapped image relates to the velocity of the nascently formed ion. This yields information on how remaining energy from a photochemical process is partitioned between its constituents. The angular distribution contains information on the dynamics of the photochemical process that formed the ion. For instance, the anisotropy in an ion image formed from a photodissociation provides information on the symmetry of the transition between ground and excited states.

1.3.2 Multi-mass Imaging

Velocity-map imaging experiments effectively comprise a time-of-flight spectrometer with a two-dimensional position-sensitive detector coupled with a camera. In the case of a single photoproduct or single desired photoproduct, all the ions can be recorded by time-gating the detector (or the camera) as the photoproducts arrive and record the velocity-mapped image.

In experiments where all photoproducts are required to be imaged, the situation is more challenging experimentally. Typical ToF acquisitions endure $\approx 100\mu\text{s}$ while ion ToF signals last 10s of nanoseconds. CCD cameras that are capable of recording multiple ion images for such a period are not widely available. Experiments can be repeated for each ion that is to be recorded, however, this is not convenient and can suffer from experimental drift. Solutions to the problem depend on the experiment and corresponding ionisation rates.

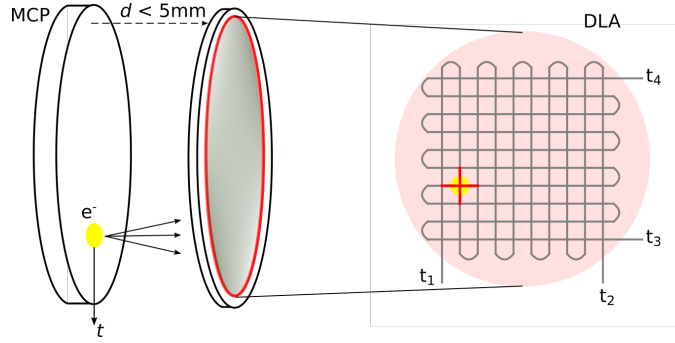


Figure 1.4: Illustration of the principle of ion detection through delay-line anode assemblies. The electron cloud produced as an ion strikes the microchannel plate (MCP) deposits charge onto the delay-line anode (DLA) assembly, which propagates along interwoven delay-lines. The time difference between the arrival times at either end of the line provides a spatial coordinate. The second spatial coordinate is determined from the second wire. The time-of-flight for an ion is determined by the initial signal at the back of the MCP.

Delay-Line Detectors

For experimental scenarios where ion count rates are low ($< 1 \text{ shot}^{-1}$), delay-line detectors are suitable for multi-mass imaging. First developed by Eland[45] in 1994, delay-line anodes are mounted behind a conventional MCP detector and aim to determine the position of the electron cloud leaving the MCP. The delay-line comprises two coplanar interwoven sets of anodes covering the area of the detector held at a constant voltage. The electron cloud deposits charge onto the two delay-line configurations and splits in both directions and propagates along the anodes. The times for each charge to arrive at the end of their respective wire is recorded and the difference in times gives the spatial coordinate. The time-of-flight is obtained from the arrival time of the photoelectron at the back of the MCP. The first delay-line anodes had timing resolutions of 1 ns and spatial resolutions of $300 \mu\text{m}$ [45, 46]. This family of detectors have a short dead-time (50 ns) before another ion can be detected.

Future generations of anode based detectors have seen improvements to the spatial ($< 45 \mu\text{m}$) and temporal ($< 100 \text{ ps}$) resolutions[47] as a result of technological advancements and improved timing methods.

Pixel-based Detectors

The development of complementary metal oxide semiconductor (CMOS) technology[48] has led to the gradual replacement of CCD technology with event-triggered CMOS sensors, such as the Pixel Imaging Mass Spectrometry (PImMS) camera[49, 50] and the Timepix3 sensor[51–54]. Such sensors employ an event-based CMOS sensor with ‘intelligent’ pixels capable of recording the position, (x, y) and time, (t) of a sufficiently intense light signal. After recording an event, a pixel has an associated ‘dead-time’ where further events cannot be recorded for a period of time. The time resolution of these sensors is the smallest time difference that a pixel can differentiate events. The spatial resolution is determined by the size of the pixel array.

Two versions of the PImMS sensor exist: the PImMS1 sensor comprises a 72×72 pixel array with a time resolution of 12.5 ns[49, 55]; the more recent PImMS2 sensor comprises a larger 324×324 pixel array with a time resolution of 25 ns[56]. Typical dead-times for each pixel is approximately 100 ns. PImMS sensors have been employed in a variety of proof-of-principle[56], VMI[57–61], and spatial imaging[50, 62, 63] experiments in a number of laboratories. The most recent Timepix sensor is the Timepix3[52, 64, 65] chip (256×256 pixel), offering an unparalleled time resolution of 1.5625 ns. Typical dead-times for each pixel in the Timepix3 chip is at least 475 ns, which is appreciably longer than the associated PImMS dead-times. The next generation of Timepix chip, Timepix4, offers substantial improvements to its predecessor. A larger pixel arrangement (512×448 pixel) will offer a much greater spatial resolution and a $8\times$ enhancement to the time resolution (≈ 200 ps). The maximum possible count rate is increased tenfold to greatly improve its throughput[66].

By integrating across all pixels, one obtains the time-of-flight spectrum for the ion imaging experiment with a timing resolution of the sensor employed. Specific velocity-map images can be obtained by extracting the (x, y) event coordinates for the time-of-flight window for an ion. Multi-mass imaging at high count rates is advantageous as one can quickly observe which ions are produced and at which velocity. The multi-mass capabilities of CMOS-based detectors is illustrated in

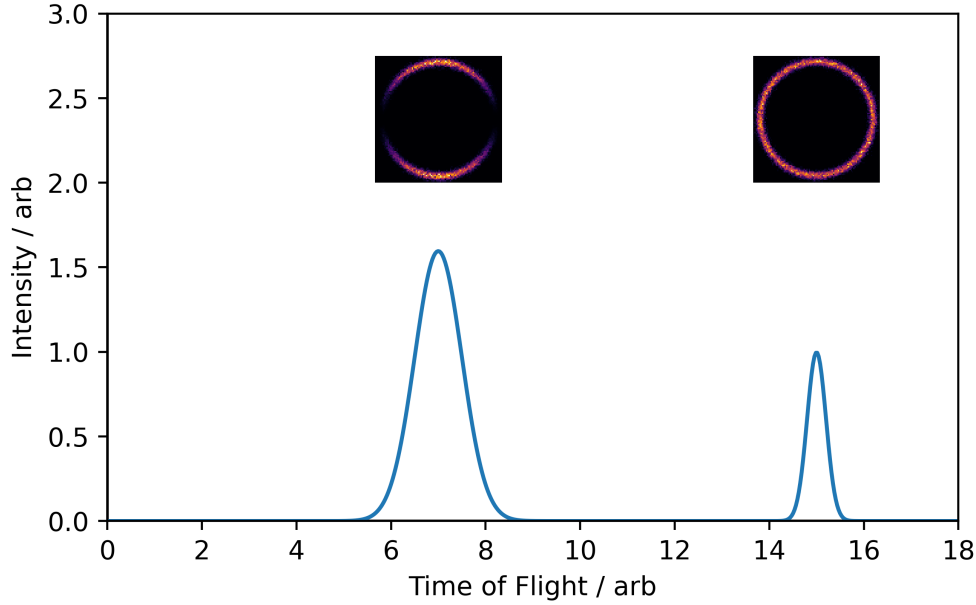


Figure 1.5: Simulated ToF profile obtainable from a CMOS-based detector, such as the PImMS camera. For each ion peak, the camera also records a velocity-map image, shown above. Both images are accumulated during the same acquisition.

Figure 1.5, which shows a simulated ToF spectrum and velocity-mapped images for each peak.

1.4 Photoproduct Correlation

Methods of particle correlation are commonly used in photoionisation experiments to achieve a deeper understanding of the underlying photochemical processes[67, 68]. In these experiments, photoproducts such as electrons and ions are detected simultaneously and correlations can be determined statistically. These correlations can reveal a multitude of information such as the population and identification of excited states[67], disentangling complex multi-photon ionisation processes[69], and angular correlation of product momenta[58, 70, 71]. There are two main approaches to determining these ion correlations experimentally: coincidence and covariance imaging. These will be discussed in the following sections. Diffraction imaging will also be discussed.

1.4.1 Coincidence Imaging

Coincidence imaging and spectroscopy[72] aims to investigate a photochemical reaction by detecting its photoproducts in coincidence, such as photoion-photoion-coincidence (PIPICO) and photoelectron-photoion-coincidence (PEPICO) imaging. These techniques can identify the origins of specific signals. Coincidence imaging is particularly useful for disambiguating three-body dissociations following Coulomb explosion, as only two species are required to fully describe the process[45, 73]. Coincidence imaging effectively relies on counting ion events and measuring the corresponding energy of each ion.

$$\text{Coinc}(X, Y) = \sum_{i=0}^{i=N} X_i Y_i \quad (1.7)$$

where X and Y are measured ion signals, such as time-of-flight, and N is the number of shots.

By minimising the count rate ($< 0.01 \text{ ions shot}^{-1}$), the assertion that two or more ion events originate from the same process becomes valid. In order to reduce the duration of coincidence experiments, high repetition-rate photon delivery systems must be used ($> \text{kHz}$). Coincidence imaging was first employed in the 1980s by Dujardin *et al.*[74] who detected two charged fragments from the same molecule in coincidence utilising photoion-photoion-coincidence (PIPICO). The most advanced method of coincidence imaging is Cold Target Recoil Ion Momentum Spectroscopy that employs reaction microscopes (REIMs) to provide highly resolved three-dimensional momentum distributions for ions and electrons[75].

Cold Target Recoil Ion Momentum Spectroscopy

Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) is a momentum imaging technique for the investigation of the dynamics of ionisation through photoabsorption, electron impact or ion impact[76]. It allows for the measurement of the full three-dimensional momentum vector of a nascent ion to a high resolution. Reaction microscopes are used for COLTRIMS experiments and are becoming increasingly popular experimental designs[77–79]. Unlike equivalent ions in VMI

experiments, ions and electrons produced in a reaction microscope are guided onto two MCP detectors by a combination of homogeneous weak electric and magnetic fields, aligned along the ToF axis. The weak electric field is not strong enough to project electrons onto the detector alone. The magnetic field forces electrons on a spiral trajectory which confines the electrons closer to the ToF axis. Despite the added complexity of the electrons' trajectories, the three-dimensional momentum can still be reconstructed. The weak extraction fields result in a greater momentum resolution[75]. Reaction microscopes employ delay-line based detectors to record the times and positions of the impact of each particle. A photodiode inside the laser system provides a reference time so flight times can be recorded as a difference[75].

1.4.2 Covariance Imaging

Covariance imaging is the emerging field originating from the innovative technique of covariance mapping introduced to photoionisation by Frasninski and coworkers in 1989[80]. Covariance mapping correlates measurements recorded at high count rates through covariance analysis. The covariance between two ion signals of interest, X and Y , is defined as the number of times are observed in coincidence

$$\text{Cov}(X, Y) = \langle XY \rangle - \langle X \rangle \langle Y \rangle \quad (1.8)$$

where $\langle XY \rangle$ estimates the average number of correlations, defined:

$$\langle XY \rangle = \frac{1}{N} \sum_{i=0}^{i=N} X_i Y_i \quad (1.9)$$

and $\langle X \rangle$ estimates the uncorrelated contributions, defined:

$$\langle X \rangle = \frac{1}{N} \sum_{i=0}^{i=N} X_i \quad (1.10)$$

where N is the number of shots.

In the regime of very low count rates, the uncorrelated estimators $\langle X \rangle, \langle Y \rangle \approx 0$, such that the covariance, $\text{Cov}(X, Y)$ converges on $\frac{1}{N} \text{Coinc}(X, Y)$.

Covariance mapping techniques are typically applied to electron ToF spectra (related to electron kinetic energies) where X and Y correspond to electron times-of-flight[69]. Throughout this thesis, covariance analysis and covariance imaging

will be employed to observe correlations between photofragments. For a full discussion, refer to Chapter 5.

1.4.3 Diffraction Imaging

Diffraction imaging is a method of probing molecular structure. Such experiments do not directly detect photofragment correlations but rather probe the atomic structure of a sample to a high spatial resolution. This allows a frozen snapshot of the molecule to be measured and thus the structure at the point of probing. Irradiation of a sample with an ultrafast electron beam[81] or an intense X-ray pulse[82–84], leads to a scattering pattern that can be imaged. The patterns can be analysed to reconstruct the molecular structure to a high spatial resolution[83]. The spatial resolution attainable is ultimately limited by the wavelength of the electrons or X-ray pulse. A common problem is the degradation of the sample due to repeated irradiation. Recent advances have led to the determination of atomic resolution structure of proteins without significant degradation from radiation damage[85] and structure of proteins have been determined to a 2.9 Å resolution[86].

Time-resolved pump-probe X-ray diffraction experiments directly record the electronic and nuclear motions during chemical or physical processes without the prior knowledge of potential energy surfaces[83]. These pump-probe experiments have been performed on proteins to study time-resolved dynamics[87].

1.5 Outline of Thesis

The work presented in this thesis primarily focusses on VMI investigations of photodynamical processes using novel techniques applied to three-dimensional imaging and covariance imaging using the PImMS2 sensor. The experimental apparatuses and principles that have been used throughout are described in the following Chapter.

Chapters 3 and 4 present a novel VMI focussing configuration for high-resolution three-dimensional imaging whose performance was verified on the well-studied one-colour photodissociation of carbonyl sulfide, OCS. Chapter 3 presents a discussion

of the novel experimental configuration and its performance. Chapter 4 presents a mathematical approach to extracting dynamical information from three-dimensional VMI images of CO photofragments.

Chapter 5 introduces in detail the concept and principles of Coulomb explosion imaging and the ionisation schemes that are employed to induce a Coulomb explosion in target molecules. Various covariance analysis techniques are also discussed and supported through simulated data.

Chapters 6 and 7 concern the pump-probe investigation of the UV-photoexcitation of thiophenone probed *via* strong-field and inner-shell ionisation, respectively. PImMS data are used to determine delay-dependent ion yields to infer photoexcitation schemes. Covariance analyses are also used to support the schemes and reveal information on the relevant dynamical processes. The ultimate goal of these experiments was to observe the UV-induced ring-opening of the parent molecule.

In Chapter 8, the Coulomb explosion of OCS molecules is investigated at varying pulse energies. The Coulomb explosion dynamics are identified through covariance analysis techniques. Chapter 9 provides a brief summary of the work presented in this thesis and presents an outlook on possible future work and directions.

2

Experimental Principles and Apparatus

In this Chapter, details of the different experimental apparatuses that have been used to collect data throughout the course of this thesis will be outlined. Experiments were undertaken in two laboratories: University of Oxford and FLASH (Free-electron Laser Facility in Hamburg) in Germany. Both of these laboratories specialise in ion imaging experiments and therefore necessarily share a number of essential components. Experimental techniques and principles will also be detailed including general analysis and data processing methods.

2.1 Experimental Principles

The data presented throughout this thesis have been collected using conventional velocity-map imaging spectrometers and experimental set-ups. Although experimental apparatuses from different laboratories vary slightly, the general concepts are similar in each case. All apparatus comprise a series of chambers kept under ultra-high vacuum conditions ($\leq 1 \times 10^{-7}$ mbar). Target molecules are introduced into the experimental chamber *via* a supersonic expansion through a pulsed or continuous valve and are passed through at least one skimmer to produce a collimated, and rotationally cold molecular beam. The molecular beam is then crossed by one or more focussed laser pulses to initiate some photochemistry and generate photoions.

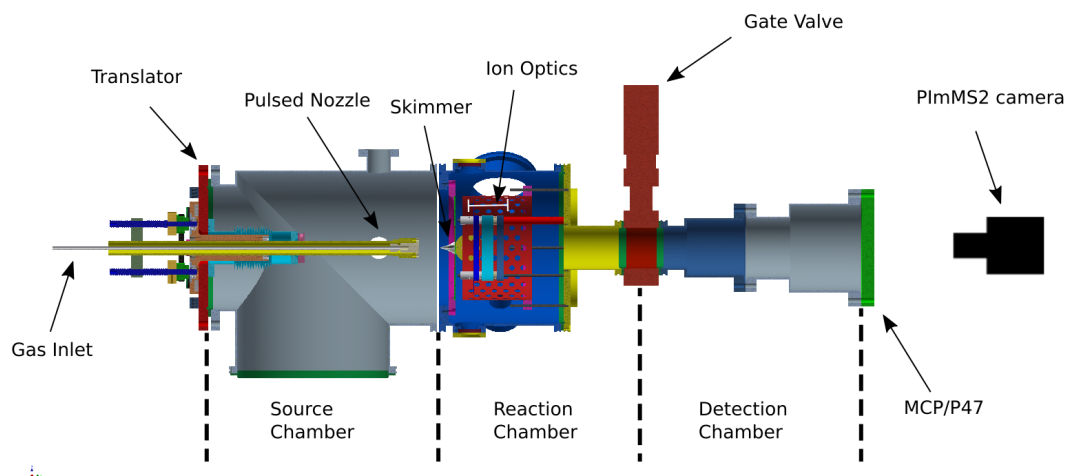


Figure 2.1: A side-on two-dimensional schematic of the Oxford VMI spectrometer. The key features are labelled. See text for a more detailed discussion.

Nascent ions are then accelerated through an electric field onto a two-dimensional position sensitive detector. The electric fields are chosen such that ions are velocity focussed onto the detector and the positions of ion events are recorded by a PImMS camera. The use of the electric field to detect ions in these experiments also separates ions by their mass-to-charge ratio, m/z .

2.2 The Oxford VMI Spectrometer

The Oxford spectrometer was used for the characterisation of Post Extraction Inversion Slice Imaging (PEISI) technique and the 3D imaging experiments (Chapters 3-4) and the Coulomb explosion imaging experiments in Chapter 8. The experiment is located in the laboratory of Professor Mark Brouard in the Chemistry Research Laboratory, Oxford. A schematic for the spectrometer is shown in Figure 2.1.

2.2.1 Overview

The spectrometer comprises three chambers: the source chamber, the interaction chamber, and the detection chamber. Each chamber is kept at ultrahigh vacuum ($\leq 1 \times 10^{-7}$ mbar). A target molecule is introduced into the chamber, typically seeded in helium, *via* a molecular beam. The gas mixture is prepared in a stainless

steel sample container fitted with a two-stage regulator set at a typical stagnation pressure of 0.5 – 2 bar. The sample preparation region is kept at a rough vacuum of 1×10^{-2} mbar by a small roughing pump (Leybold D4B). This also prevents corrosion of the gas line when the experiment is not in use. The sample mixture is subsequently supersonically expanded into the source chamber through the nozzle of a pulsed (10 Hz) General Valve (Series 9). This generated a molecular beam with a rotational temperature, T_{rot} of < 25 K [71, 88, 89]. The General Valve is mounted onto the experimental chamber such that the molecular beam can be translated three-dimensionally to optimise the experimental signal.

The source chamber is pumped by a 600 L s^{-1} turbomolecular pump (TMP), backed by an Edwards three-wave rotary pump. With no molecular beam, background pressures in this chamber are typically around 1×10^{-7} mbar, increasing to around 1×10^{-6} mbar under experimental conditions.

The source chamber is separated from the interaction chamber by a 1 mm (diameter) skimmer (Beamdynamics Ltd.). The target molecule supersonically expands through the skimmer to produce a collimated molecular beam. The interaction chamber houses the experimental ion optics assembly and is pumped by a 600 L s^{-1} TMP (Alcatel ATP 400) backed by a rotary pump (Leybold, Trivac D40V) to a typical background pressure of 5×10^{-8} mbar, rising to 1×10^{-7} mbar under experimental conditions. The molecular beam is intersected by a laser pulse in the interaction region of this chamber.

The flight tube is separated from the interaction chamber by a gate valve and is pumped by a small TMP (Pfeiffer Vacuum TMU 071P) backed by the same Leybold Trivac D40V rotary pump that backs the interaction chamber. The gate valve allows for the detection chamber to remain isolated at vacuum from the rest of the experimental chamber during maintenance that requires atmospheric pressure. This protects the sensitive detector from exposure to atmospheric pressure and vapours. The detection chamber is particularly sensitive to stray fields as the ions are no longer accelerated. A double-layered, cylindrical μ -metal magnetic shield

was installed in the flight tube to minimise the effect unwanted electromagnetic fields may have on photoions and photoelectrons in this region.

2.2.2 Ion Optics

The ion optics assembly is mounted on the main flange of the interaction chamber by four stainless steel rods, shown in Figure 2.2. The ion optics consist of a stack of 1 mm thick circular stainless steel plates, with a central aperture of increasing size through which ions pass. The size of each aperture was chosen for optimal velocity mapping conditions. Each ion optic plate is electrically isolated from each other by MACOR[®] spacers. In this thesis, two ion optic configurations have been used to accommodate either DC slicing (Chapters 3 and 8) or Post Extraction Inversion Slice Imaging (PEISI) (Chapters 3-4). In DC slicing, the ion optic configuration comprises three charged plates and a fourth grounded plate. The first three plates, the repeller, extractor, and third lens, are held at a constant voltage provided by two high voltage supply units *via* three high voltage feedthroughs (supplied by KING) that are mounted on a DN40 flange fitted to the external wall of the interaction chamber. The feedthroughs are connected to its corresponding ion optic plate by a crocodile clip.

In PEISI experiments, two additional electrodes, a charged plate and a grounded grid, are introduced. MACOR[®] spacers are used to separate the first grounded plate and the additional two plates. The second grounded plate has a fine mesh grid that decreases the transmission of ions but reduces ion distortions. This plate is grounded through connection to the back wall of the interaction chamber. This ensures that there is no unwanted accumulation of charge at the plate. The first plate was supplied with high voltage through a high voltage MOSFET switch (Behlke, HTS 121, 12 kV, 30 A) so that the voltage may be applied to the plate on a short timescale (≈ 40 ns) to implement the Post Extraction high voltage pulse necessary for PEISI conditions. A high voltage feedthrough (SHV-10) mounted on another external wall of the interaction chamber connects the pulsed plate to the

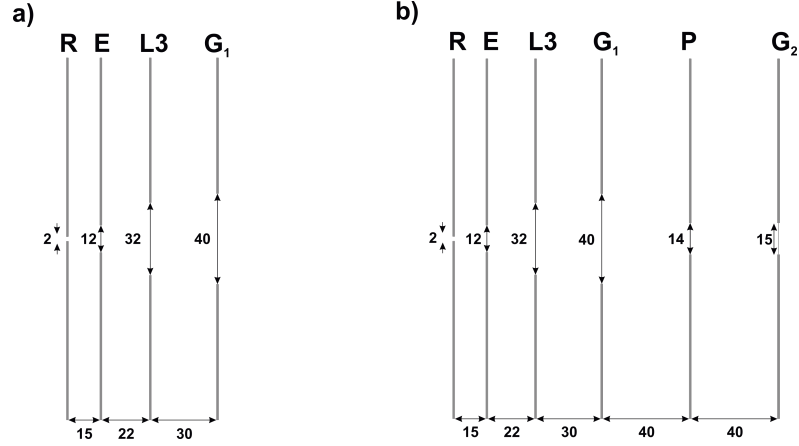


Figure 2.2: Schematic of the ion optic configurations employed for the course of this thesis. a) DC slicing configuration; b) PEISI configuration. R, E, L3, G_i , P correspond to the repeller, extractor, third lens, grounded plates, and pulsed electrodes, respectively. All measurements are given in mm. See Chapter 3 for more details. Figure adapted from Reference [90].

pulsed high voltage supply unit. The MOSFET switch was connected to a delay pulse generator to synchronise the timing with the experiment.

2.2.3 Detector

The detection assembly is comprised of a pair of 75 mm chevron-stacked MCPs coupled to a P47 phosphor screen. The MCPs have a pore diameter of $25\ \mu\text{m}$ and a pitch of $32\ \mu\text{m}$, giving a theoretical open area ratio (OAR) of 55.4%. Ions impinging on the detector result in the emission of electrons. A large potential difference (typically 1.9 kV) is held between the front and back faces of the MCPs. Electrons are accelerated across this region and produce more electrons at each interface. The final electron cloud is accelerated onto the phosphor screen (P47) operating at typical potential differences of 4 kV. The phosphor screen emits flashes of light which are subsequently recorded by the PImMS2 camera as an x, y coordinate and corresponding time-of-flight, t . Occasionally, a photomultiplier tube (PMT) is used to measure the flashes of light emitted from the phosphor screen. The PMT was connected to an oscilloscope (Techtronix) to obtain a time-of-flight trace.

2.2.4 Optical Systems

The experiments outlined in this thesis using the Oxford spectrometer were performed using one of two laser systems. The 3D imaging experiments presented in Chapters 3-4 employed a nanosecond pulse system, while the Coulomb explosion imaging experiments presented in Chapter 8 employed a femtosecond pulse system.

Nanosecond Optical System

The UV radiation used for the photodissociation of OCS was produced by a dye laser system (Sirah, Cobra Stretch) pumped by the third harmonic of a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Continuum, Powerlite Precision II), operating at 10 Hz. The maximum third harmonic pulse energy of the Nd:YAG laser was approximately 300 mJ. This was attenuated to the desired level by adjusting the time delay between the flashlamps and the Q-switch of the laser. The dye solution used was Coumarin 460 dissolved in methanol. The frequency doubled output was produced using a BBO type I crystal (SHG 220) and was separated from the fundamental by a set of four Pellin-Broca prisms. The beam was then steered to the experiment using five optical prisms and focussed into the interaction chamber through a UV fused silica window, using a 20 cm focal length lens.

Femtosecond Laser at Oxford

The Femtosecond Laser at Oxford (FLO) (Solstice Ace, Spectra Physics) is a Titanium:Sapphire (Ti:Sa) laser system which produces infrared (centred at 800 nm) laser pulses with an average power of 5 W. This laser system consists of an oscillator, regenerative amplifier, and a compressor. The key specifications of FLO are outlined in Table 2.1.

The oscillator consists of a Ti:Sa crystal contained in a cavity which is pumped by a frequency doubled nanosecond Neodymium-doped yttrium orthovanadate (Nd:YVO₄) laser at 532 nm. The oscillator is mode locked[91] and produces a train of ultrashort pulses at a repetition rate of 80 MHz. These pulses are broadband and with a very low energy (nJ) and must be amplified further to be used experimentally.

Central Wavelength	Bandwidth	Pulse Duration	Average Power	Rep Rate
800 nm	60 nm	35 fs	5 W	1 kHz

Table 2.1: Key specifications of FLO based on factory specifications.

The pulses from the oscillator are amplified using Chirped Pulse Amplification (CPA)[92] in a regenerative cavity. During CPA, the laser pulse is stretched temporally which reduces the peak power sufficiently such that they can be amplified to high pulse energies without damaging the optics. The amplifier consists of a Ti:Sa crystal pumped by a Neodymium-doped yttrium lithium fluoride (Nd:YLF) nanosecond laser, that runs at a repetition rate of 1 kHz. The seed pulse passes through the Ti:Sa crystal several times, extracting more energy from the crystal on each pass. After all the energy from the crystal has been extracted, the high energy pulse (5 mJ) pulse is sent into a compressor. The compressor compresses the stretched, amplified pulse back to an ultrashort (nominally 35 fs) pulse, which are then used experimentally.

After arriving on the laser table the laser pulse is attenuated by a 20/80 beamsplitter (Thorlabs UFBS2080). The 80% part is directed into a beam dump. The remaining pulse is directed onto an ultrafast variable attenuator (Newport VA-800). A $1/2$ -waveplate variably changes the polarisation of the vertically polarised output of the Solstice Ace, depending on how the waveplate is adjusted. A thin-film polariser (TFP) separates the polarisations of light, and the horizontal polarised light is discarded. The laser pulse duration is lengthened by this process. The remaining vertically polarised light then passes through a 50/50 beamsplitter (Thorlabs UFBS5050). One half is directed toward a diagnostic table and will be discussed shortly. The other half passes through a second 50/50 beamsplitter (Thorlabs UFBS5050). One half of this pulse is directed onto a power meter (Thorlabs S142C), which records the pulse energy. The other half passes through a periscope and a combination of silver mirrors before arriving at a focussing lens (20 cm focal length), where it is focussed at the interaction region within the

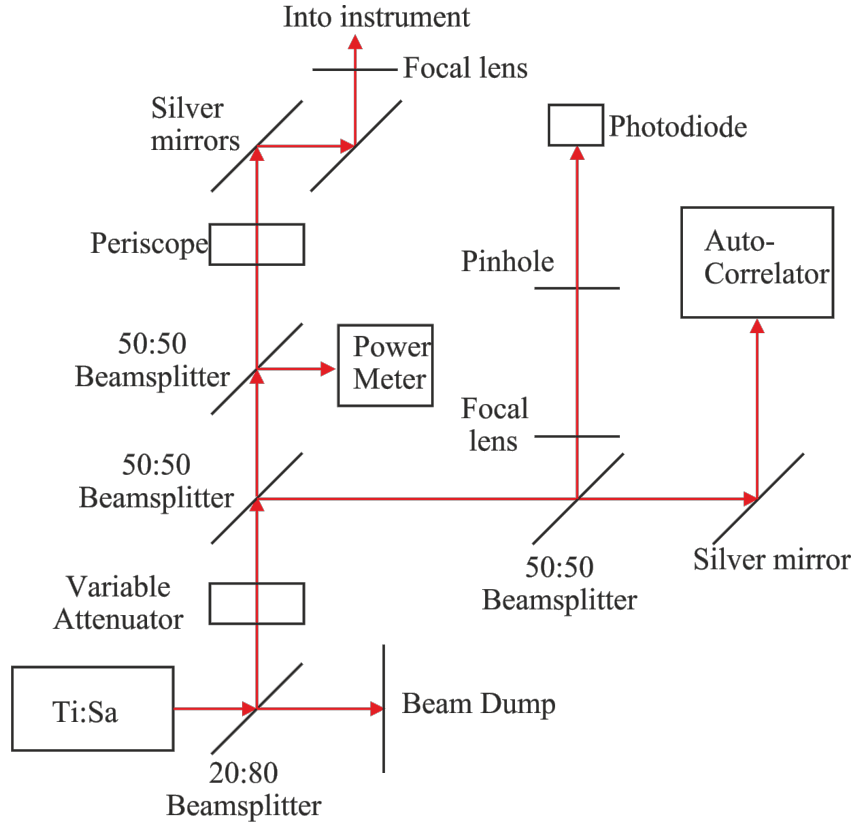


Figure 2.3: The beam path of FLO on the laser table after exiting the Solstice Ace. See text for more details.

experimental chamber. The pulse then passes through the window on the opposite side of the spectrometer where it is dumped.

The aforementioned diagnostic beam passes through a second 50/50 beamsplitter (Thorlabs UFBS5050). One part is directed through an identical focal lens that the light passes through before entering the experimental chamber. The light then travels to a photodiode which is connected to an oscilloscope. A $1\mu\text{m}$ pinhole is placed in between the photodiode and the focal lens 20 cm from the focal length. The pinhole can be gradually moved across the path of beam while recording the current measured by the photodiode. This gives an estimate of the focussed beam spot diameter to estimate pulse intensities. The second part is reflected by a silver mirror into an auto-correlator (Pulse Check) that determines the pulse duration of the laser pulse. The beam path of the laser pulse on the laser table is summarised in Figure 2.3. Typically, during alignment FLO was operated at the maximum

repetition rate of 1 kHz. During data acquisition this was reduced to 10 Hz in line with the repetition rate of the PImMS camera and the molecular beam.

2.3 The FLASH VMI Spectrometer

The double-sided FLASH spectrometer was used for the pump-probe experiments undertaken at the free-electron laser facility at Hamburg (FLASH) in Chapters 6 and 7. The spectrometer is used to focus ions and electrons from the interaction region onto two detectors[93, 94].

2.3.1 Overview

The spectrometer is connected to the permanent CFEL-ASG Multi-Purpose (CAMP)[42, 93] experimental endstation that was used at Beamline 1 (BL1) at FLASH in Hamburg, Germany. The CAMP experimental endstation is connected to the FEL beam and is coupled to the FLASH1 pump-probe laser system, before both laser pulses enter the main experimental chamber. The schematic of the CAMP chamber is displayed in Figure 2.4.

A pulsed molecular beam of target molecules (seeded in xenon) was generated using a pulsed Even-Lavie valve[95]. The beam of the target molecule is collimated through two skimmers of diameters 2 mm and 4 mm, respectively (both Beamdynamics Ltd.) before it is introduced into the CAMP endstation where it is orthogonally crossed by up to two of three laser pulses in the middle of the double-sided spectrometer: the third-harmonic ($\lambda = 267$ nm) or fundamental ($\lambda = 801$ nm) output of the in-house Ti:Sa laser, or the XUV output ($\lambda = 6.3$ nm) of the FEL. The FEL beam enters the CAMP chamber and is coupled to the FLASH1 pump-probe laser system. Both laser pulses then enter the main experimental chamber where the FEL is notionally focussed into the centre of this region. The final focus position of the FEL cannot be changed. To obtain spatial overlap between the optical lasers and the FEL, the CAMP chamber is on a frame that can be translated in the XYZ direction as well as pitched and tilted with respect to the FEL beam. Thus, the chamber can be moved such that the laser pulses are spatially aligned.

Interaction of the molecular beam and the laser pulses produced ions and electrons. The double-sided VMI spectrometer allows for the simultaneous detection of both. Both sets of ions are recorded by one of two two-dimensional position-sensitive detectors. The ion and electron detectors consisted of a pair of MCP stacks and a phosphor screen (P47). Flashes of light emitted from the ion detector P47 were recorded by a PImMS2 sensor. Flashes of light emitted from the electron detector were recorded by a conventional VMI charge-coupled device (CCD) camera.

Spatial Overlap

Spatial overlap of the optical and FEL pulses is paramount to successful pump-probe experiments to ensure that the same target molecules are interacting with both pulses. This is achieved at FLASH by ionising a pulsed molecular beam of a seed gas, such as xenon, under spatial mapping conditions with the optical laser and FEL. Under spatial mapping conditions, the position of the ionised gas is mapped onto the detector. The spatial focus of the FEL cannot be changed so the spatial focus of the optical laser is altered until the foci overlap. To do this, the CAMP chamber is on a frame that can be translated in the XYZ direction as well as pitched and tilted with respect to the FEL beam. Thus, the chamber can be moved such that the laser pulses are spatially aligned. The position of the spatial focus of each laser is monitored with PImMS. The CAMP chamber is then iteratively moved until spatial overlap is fully achieved.

Temporal Overlap

Temporal overlap of the two laser pulses is also very important for pump-probe experiments. Experiments must be performed around meaningful pump-probe delays *i.e.* before and after temporal overlap. If a good temporal overlap is not achieved, it is impossible to accurately know the pump-probe delays. Temporal overlap can be found in many ways. One method is to perform pump-probe (IR-FEL) experiments with xenon and monitor the ratio of yields of Xe^{2+} ions and Xe^{3+} ions as a function of delay. The ratio decreases when the FEL precedes the IR pulse as the IR pulse post-ionises metastable Xe^{2+} ions formed following

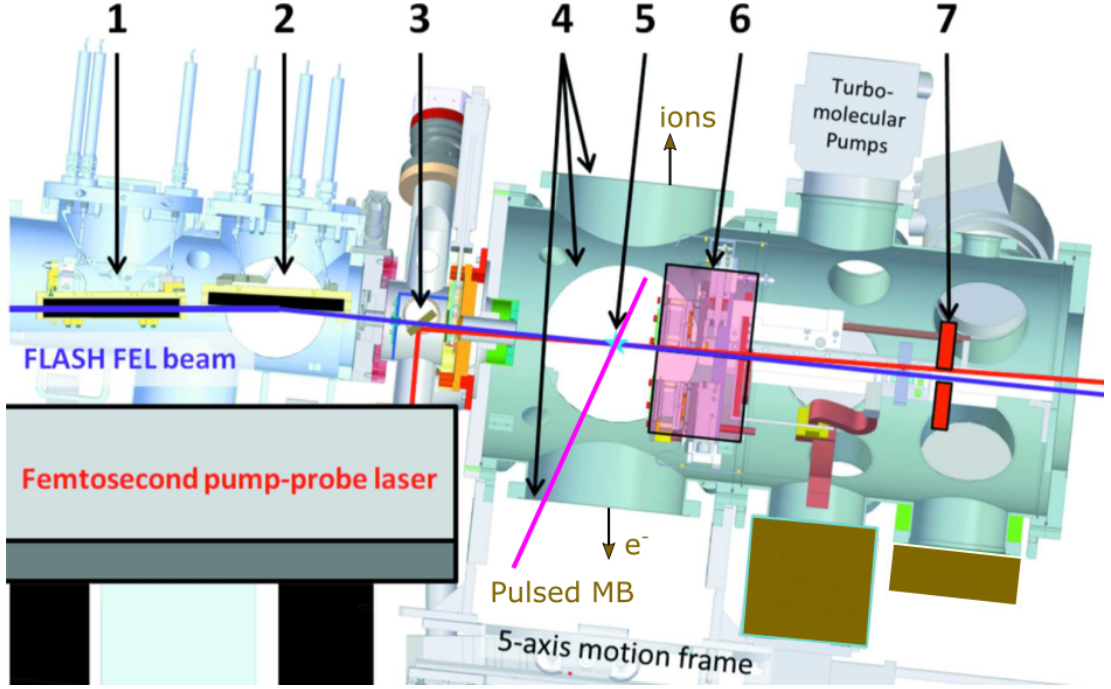


Figure 2.4: Schematic of CAMP[42]. Arrows (1) and (2) are horizontal and vertical focussing mirrors. Arrow (3) shows where the XUV and optical laser pulses are coupled through a holey mirror. Arrow (4) shows the main experimental chamber to which the spectrometers are attached. Arrow (5) shows the focal point of the XUV and optical laser pulses and the intersection with the molecular beam. Arrows (6) and (7) show possible detector locations. In these experiments, the double-sided VMI spectrometer was attached either side of the interaction region. Ions and electrons are extracted in the directions labelled.

Xe (4d) ionisation and Auger decay[96–98]. The delay-dependent ratio can be fit to a normal cumulative distribution function to yield the temporal overlap, t_0 , between the IR and FEL pulses[61].

2.3.2 Ion Optics

A double-sided spectrometer was employed in the FLASH experiments[42, 93]. As mentioned previously, the spectrometers are connected above and below the CAMP endstation. As a result, the ToF axis lies perpendicular to the plane of the propagation of the molecular beam and the laser pulses. Oppositely polarised electric fields focus the ions and electrons onto two position-sensitive particle detectors.

2.3.3 Detector

The detection assembly for both ions and electrons comprise a pair of chevron-stacked MCPs coupled to a phosphor screen. The ion detector comprises a pair of 80 mm chevron-stacked MCPs coupled to a P47 phosphor screen. The electron detector comprises a pair of 40 mm chevron-stacked MCPs coupled to a P20 phosphor screen. There was a potential difference of around 2300 V across the front and back faces of the MCPs and a potential difference of around 3800 V across the phosphor screen.

The ion detector has an analogue-to-digital current (ADC) readout connected to the back of the MCP stack. The ADC records the change in current across the MCP stack as ions hit the detector. This signal is converted to a digital signal and stored on the FLASH DAQ. The timing precision of the ADC readout is 500 ps. This enables high-resolution ToF spectra to be recorded.

2.3.4 Optical Systems

The pump-probe experiments outlined in this thesis that employed the FLASH spectrometer were performed using two laser systems: the FLASH1 optical titanium:sapphire (Ti:Sa) laser system and the FLASH free-electron laser (FEL). In Chapters 6 and 7, the third harmonic of the fundamental of the Ti:Sa laser system provides the pump pulse ($\lambda = 267$ nm) that initiated some photochemistry in the target molecules. The probe pulse in Chapter 6 is the fundamental 800 nm pulse generated by the Ti:Sa laser system operated at 10 Hz. The probe pulse in Chapter 7 was a 6.3 nm (197 eV) XUV pulse provided by the FLASH FEL.

Titanium:Sapphire Laser System

The infrared (IR) 810 nm (70 fs (FWHM); $I_0 = 2 \times 10^{14}$ W cm⁻²) pulse was generated by the in-house Ti:Sa laser system, operated at 10 Hz. Laser pulses are amplified to 20 mJ by a commercial chirped pulsed amplifier (CPA) system, which consists of a regenerative and a 2-pass amplifier (Hidra-25, Coherent)[99]. The IR beam passes through a beam splitter so that the reflected beam can be frequency-tripled with non-linear beta barium borate (BBO) crystals without affecting the transmitted beam.

The resulting 800 nm laser pulse has a maximum pulse energy of 3.5 mJ, minimum pulse duration of 70 fs at a repetition rate of 10 Hz. The intensity of this unfocussed laser pulse was around $2 \times 10^{14} \text{ W cm}^{-2}$.

The 267 nm (150 fs (FWHM); $I_0 = 7 \times 10^{12} \text{ W cm}^{-2}$) was generated from the frequency-tripled output of the fundamental laser pulse, with a measured pulse energy of around 35 μJ . The ultraviolet (UV) laser pulse was temporally compressed to around 150 fs using a prism compressor and focussed into the chamber using a telescope with a beam width of approximately $40 \mu\text{m} \times 40 \mu\text{m}$. These values return a peak intensity of around $7 \times 10^{12} \text{ W cm}^{-2}$ and should therefore not be in the strong-field ionisation regime.

These laser pulses were rejoined and temporally coupled using a delay stage. The delay stage was also used to vary the pump-probe delay between the two laser pulses.

The Ti:Sa shares a master clock with the FLASH FEL, this ensures that the pump-probe laser experiments can be performed with the FEL.

2.3.5 Free-electron lasers

Free-electron lasers (FELs) are accelerator-based lightsources that can generate [100–105] intense ($10^{12} - 10^{14} \text{ photons pulse}^{-1}$), ultrashort ($2 - 300 \text{ fs}$) pulses in the XUV range ($0.12 - 52 \text{ nm}$)[103, 106].

As the name suggests, FELs start with a beam of electrons. A picosecond laser irradiates a photocathode to generate a very short and intense electron beam[107]. These electrons are accelerated to relativistic velocities through a superconducting linear accelerator. Electromagnetic radiation can be extracted from the kinetic energy of the electron beam by passing the electron beam through a series of alternating magnetic fields, known as an ‘undulator’. This interaction causes the electron beam to undulate perpendicularly to the magnetic fields and thus emit radiation. The central wavelength of this radiation is related to the characteristics of the alternating magnetic fields and the kinetic energy of the electron beam[102].

The broad band, incoherent radiation emitted from the electron bunch necessarily travels ahead of the electron beam which interacts with it as it follows. Only

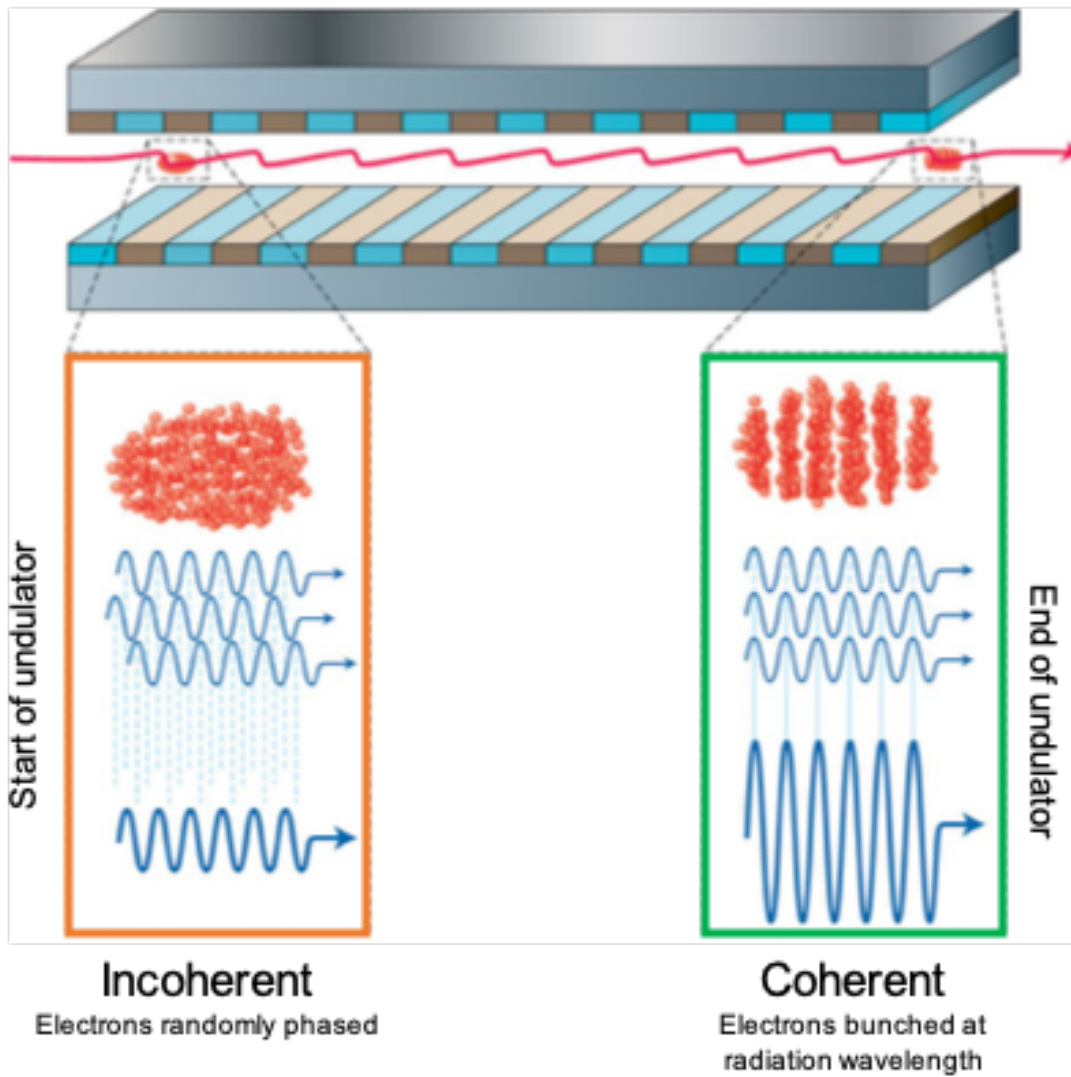


Figure 2.5: The working principle of a free-electron laser based on superconducting accelerator technology is illustrated here. See text for detailed description. Adapted from Reference [102].

wavelengths of radiation that are an integer number of fundamental wavelengths will constructively interfere after many undulator periods. Other wavelength components are ultimately destroyed. As a result, the electron beam is strongly bunched at the fundamental wavelength by the end of the undulator. This is known as ‘microbunching’[102] and is described in Figure 2.5[102]. As the electron beam enters the undulator (orange box) the phase of the electrons is random and therefore the emitted radiation is incoherent. As the electron beam passes through the undulator, only in-phase electrons undergo constructive interference and when the electron

beam leaves the undulator, the electron bunches are separated by the fundamental wavelength, resulting in coherent radiation of the fundamental wavelength. This process is known as self-amplified spontaneous emission (SASE)[101, 102, 108]. The fundamental wavelength can be tuned by changing the initial energy of the electron beam and the undulation parameter. As FELs produce laser pulses from noise, the characteristics of each laser pulse, such as pulse energy and delivery time of the XUV pulse, are inherently unstable and therefore fluctuate on a shot-by-shot basis.

FLASH FEL

The Free-electron laser facility at Hamburg (FLASH FEL)[93] is a free-electron laser capable of producing XUV pulses of 10^{13} photons/pulse with a pulse duration of 10 – 15 fs[101, 109]. For the experiments presented in Chapter 7, the FLASH FEL was operating at an average electron energy of 1.03 GeV in single-bunch mode with 700 pC bunch charge, operating at 10 Hz. The resultant XUV pulses had a central wavelength of 6.30 ± 0.01 nm (197 eV), a pulse energy of 37.5 ± 7.5 μ J, and an average pulse width of 39 ± 2 fs. Figure 2.6 shows the typical variation in the electron train energy (Panel A), photon wavelength (Panel B), photon energy (Panel C), and pulse width (Panel D) for an FEL experiment performed at FLASH.

2.4 FLASH Diagnostic System

Free-electron lasers produce laser light through the inherently stochastic Self-amplified spontaneous emission (SASE)[101, 108] process. One key result of SASE is that the characteristics of the resultant laser pulses fluctuate randomly on a shot-by-shot basis. This can be observed in Figure 2.6 where the distribution of four such laser parameters are shown. The randomness of the FEL pulses results in an uncertainty as to the exact characteristic of a particular laser pulse. The pulse energy and timing information are particularly crucial characteristics to be confident of when analysing FEL data. A laser pulse with a higher pulse energy produces more ions, which could erroneously be attributed to a feature of the photochemistry. Similarly, a laser pulse that arrives relatively later or earlier

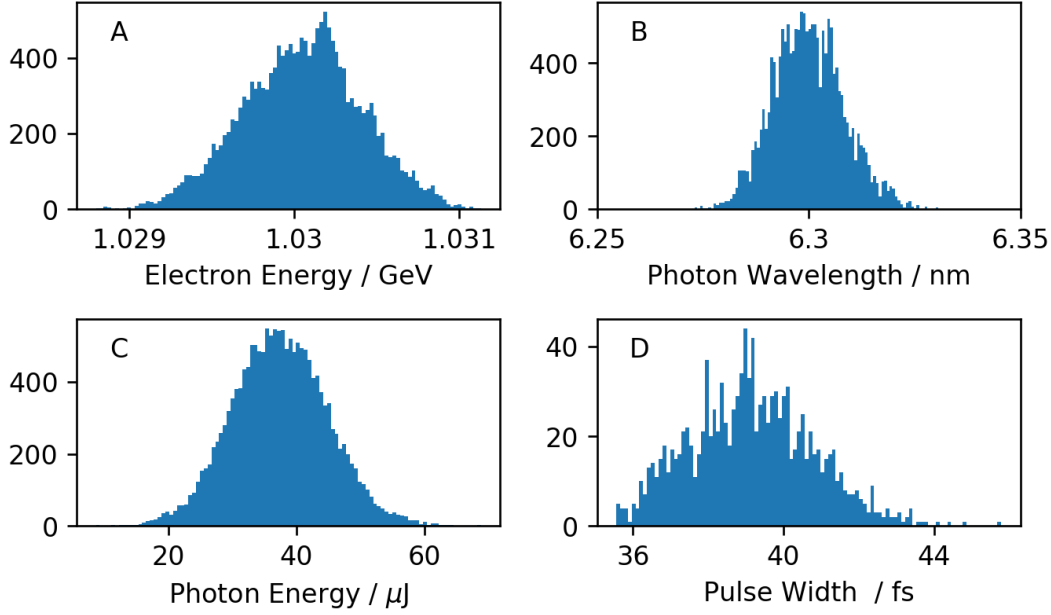


Figure 2.6: The distribution of some of the fluctuating parameters that vary on a shot-by-shot basis during FLASH experiments. Panel A shows the energy of the electron bunch at the end of the undulator. Panel B shows the photon wavelength. Panel C shows the photon energy: a broad distribution of photon energies is observed which effects the number of ions that are produced. Panel D shows the full-width at half-maximum (FWHM) of the XUV pulse produced by the FEL.

that expected could result in artefacts in the experimental data. Fortunately, the FLASH diagnostic system has been designed to record as many parameters of each FEL pulse as possible[107]. These parameters are recorded concurrently to the experimental data and are synchronised such that fluctuations can be reliably accounted for. Other fluctuations that can be accounted for include the final direction the FEL pulse points (x -, y - pointing positions) and the synchronisation of the FEL timing to the pump-probe delay stage.

In the pump-probe UV-FEL data presented in this thesis, the pulse energy, the timing jitter, and large fluctuations in the delay of the optical laser system were accounted for. The specific parts of the diagnostic system that record these parameters will be discussed in the following sections[107].

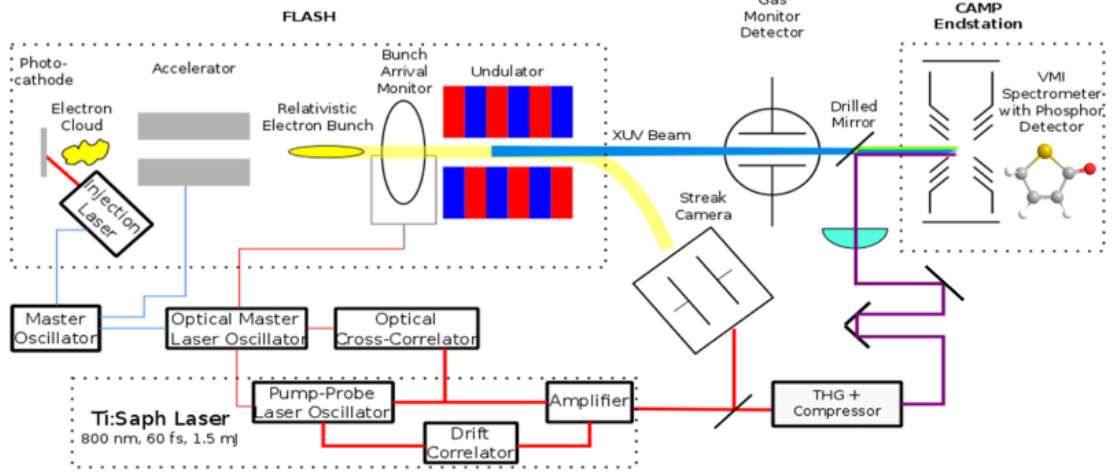


Figure 2.7: A detailed sketch of the FLASH FEL, the in-house Ti:Sa laser, and key features of the FLASH Diagnostic system. Adapted from Reference [107].

2.4.1 Gas Monitor Detection

The gas monitor detector (GMD)[110] measures the XUV pulse energy for each FEL shot. The GMD is placed behind the SASE undulators before the FEL pulse arrives in the chamber, as shown in Figure 2.7. Here, the XUV beam passes through an ionisation chamber filled with xenon, at a pressure of $\sim 2 \times 10^{-6}$ mbar. At these pressures, 99% of the XUV beam is transmitted so as not to significantly affect the number of experimental photons, while there is sufficient generation of photoions and photoelectrons to produce a current that can be converted to an XUV pulse energy.

2.4.2 Bunch Arrival Monitor

The timing system of the FLASH linear accelerator is controlled by the master oscillator (MO). The MO synchronises the generation of the initial electron cloud (injector laser), the accelerator, and the optical master laser oscillator (MLO). The MLO controls the delay stage of the optical laser system and thus these allow synchronisation between the pump and probe delays. The Ti:Sa laser is actively stabilised to the MLO at 10 kHz with an all-optical feedback system[111]. With this stabilisation active, the synchronisation between the actual optical delay and the reference delay is less than 10 fs (RMS)[111].

However, pump-probe experiments that have employed the FEL have an added jitter that significantly affects the temporal resolution of the pump-probe laser delays. This jitter derives from random variations in the electron bunch arrival time. These variations arise from fluctuations in the electron bunch energy and hence varying flight times through the compressors in the accelerator. These fluctuations cause the delivery of the XUV pulse to vary by up to 100 fs (RMS)[107] relative to the pump-probe delay that the MLO has measured.

In order to measure this arrival-time jitter between the electron bunch arrival time in the accelerator and the MLO, several bunch arrival monitors[112] (BAMs) are installed along the FEL pathway. Within each BAM, the electrical transient signal of the electron bunch is recorded. This signal is compared to the amplitude of the laser pulse from which the relative arrival time can be determined on a shot-by-shot basis[107]. With optimal FEL parameters for monitoring the bunch arrival times, the resolution of the relative arrival time can reach 5 fs[112].

2.4.3 Streak Camera

For technical practicalities the BAMs can only measure relative discrepancies of up to 4 ps. For timing drifts of greater than 4 ps, the BAM automatically adjusts in order to stay in the measurement window[107]. These long term drifts can be measured by a streak camera[99] (Hamamatsu C5680). The streak camera monitors the time delay between the output of the optical laser and the dipole radiation emitted by the electron bunch as it travels through a magnet to split the electrons from the XUV photons. The streak camera has a working time window range of 80 ps and can therefore be used to monitor long time drifts between the two laser pulses. The resolution of the correction made by the streak camera is typically around 200 fs.

As this correction has a lower resolution than the BAM correction, in pump-probe delays where these drifts are significant it is often more practical to delete the corresponding shots. These long time drifts typically last for fewer than 100 shots and therefore this does not represent a significant loss of statistics and ensure the fidelity of the pump-probe delay assignment.

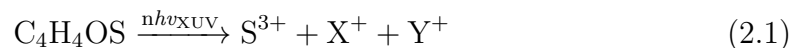
2.4.4 Illustrative Example

The following section will outline the correction process for a typical ion channel from the UV photoexcitation ($\lambda = 267$ nm) of thiophenone probed with an XUV pulse ($\lambda = 6.3$ nm) delivered by the FLASH FEL (discussed in Chapter 7). The XUV wavelength was chosen to coincide with the large sulfur (2p) cross-section[113] (see Chapter 5 for more details). Therefore this site is preferentially ionised and the overall effect of this is that highly charged sulfur cations are produced. The ion images considered here relate to the S^{3+} fragment produced from a series of pump-probe experiments.

These experiments were performed at a sufficiently high UV intensity that the proceeding interaction with thiophenone was in the regime of multi-photon absorption. As a result, the UV pulse prevalently dissociated the thiophenone target molecules in addition to any ring-opening.

There are a number of dissociation pathways that can result from the photon interactions. Panel A of Figure 2.8 show the delay-dependent radial distribution of inverted S^{3+} ion images (after corrections have been applied). At negative pump-probe delays, the UV pulse arrives after the XUV pulse (UV Late delays) and at positive pump-probe delays, the UV photon arrives before the XUV pulse (UV Early delays).

The high kinetic energy region marked I in the Figure corresponds to the Coulomb explosion of intact thiophenone molecules. The XUV pulse produces the S^{3+} ion and one or more charged fragments on the molecule that results in the formation of high kinetic energy ions. This feature is apparent at all pump-probe delays as there is always some intact target molecules and the UV pulse has no effect on the feature.



Equation (2.1) generalises this channel where ions X and Y could be a number of ions that result from the fragmentation of the Coulomb explosion.

Second, the UV pulse can dissociate thiophenone:



Equation (2.2) summarises this channel where thiophenone is dissociated into neutral sulfur and one or more neutral cofragments. In general, these fragments could be ionised.

The dissociated fragments move apart and at a later pump-probe delay (UV Early) the XUV pulse ionises the sulfur. For this channel, the sulfur absorbs two XUV photons resulting in the triply charged cation and the cofragment X is also ionised. This leads to an increase in their kinetic energy from the additional energy as a result of the repulsion between the two charged species. This is marked (II) in Panel A. With increasing pump-probe delay, the distance between S and X increases and therefore the additional Coulombic energy decreases resulting in the ‘Coulomb curve’ apparent (marked (II) in Panel A and is generalised in Equation (2.3)).



Panel C plots the (corrected) ion yield of S^{3+} in Channel II (blue crosses) and its corresponding fit (red dashed line). The ion yield has been fitted to an exponential rise function:

$$y(t) = A \left[1 - \exp\left(-\frac{t - t_0}{\tau}\right) \right] + y_0 \quad (2.4)$$

where $y(t)$ is the yield of low kinetic energy of S^{3+} ions at a pump-probe delay, t , τ is the exponential rise time, A is the amplitudes of the exponential rise function, and y_0 is the baseline intensity of ions.

Figure 2.9 shows stages of corrections as applied to the discussed Channel. Panel A shows the delay-dependent ion yield normalised by total shots comprising each pump-probe delay bin and the corresponding fit to Equation (2.4). The ion yield shows a sharp increase at +1 ps and a further increase at ≈ -1.5 ps. The second increase appears reasonably suddenly which suggests that the pump-probe delays are not correct. There are also a number of data points that appear to be clearly

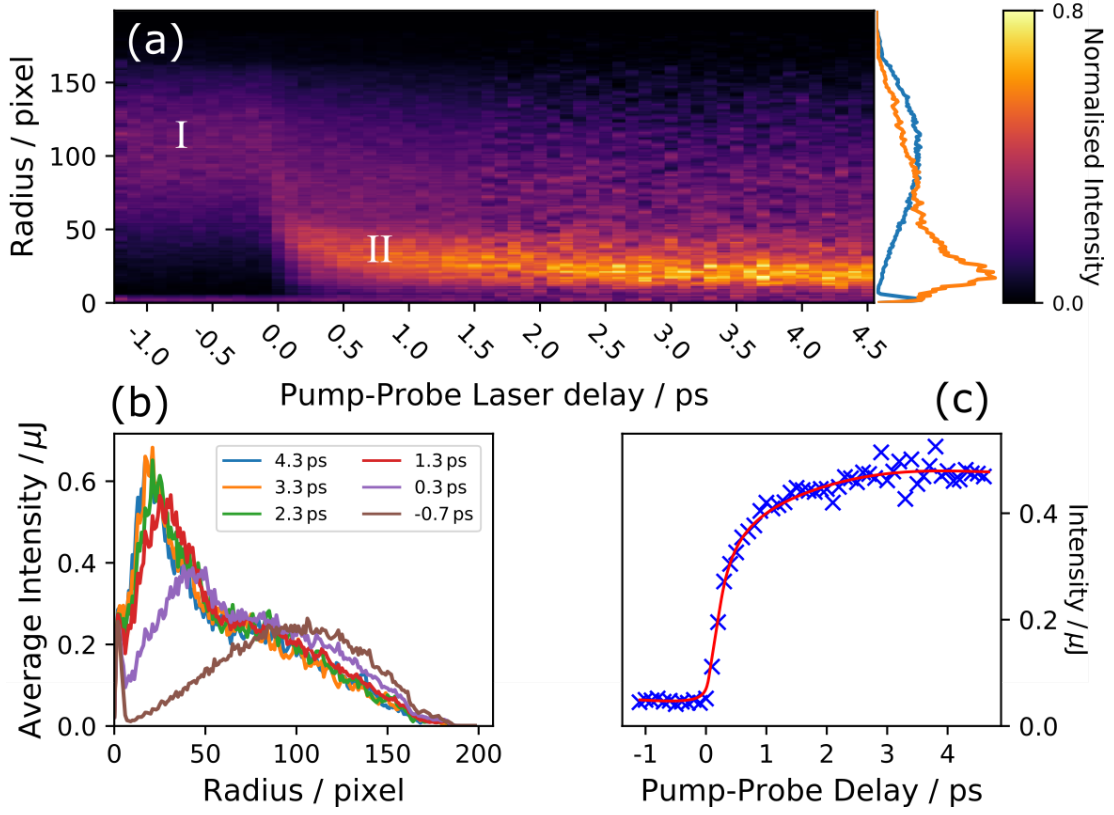


Figure 2.8: Panel A shows the delay-dependent radial distribution of Abel inverted S^{3+} ion images. Channels I and II are labelled on the distribution and their respective origins are discussed in the text. Panel B show radial distributions at different delays. Channel II is not visible at UV late delays but becomes increasingly important at UV early delays. Panel C shows the delay-dependent ion yield of Channel II S^{3+} ions after a complete correction of the data. See text for more details.

at the wrong pump-probe delay. Panel B shows the same plot except each delay bin has been normalised to the total pulse energy comprising the delay bin. This has not had a significant change to the shape of the experimental yield. This is because the pulse energy did not significantly permanently increase or decrease during these experiments and therefore the normalisation is similar to the total number of shots. Panel C shows the ion yield where the pump-probe delays have been rebinned according to the BAM value of each laser shot. This significantly improves the shape of the ion yield and there are no obvious outliers in the intensity of the pump-probe. The sharp increase that occurred with the onset of Channel II ions is diminished and now represents a more gradual and realistic appearance of these ions. Panel D shows the equivalent plot except the dataset has had shots

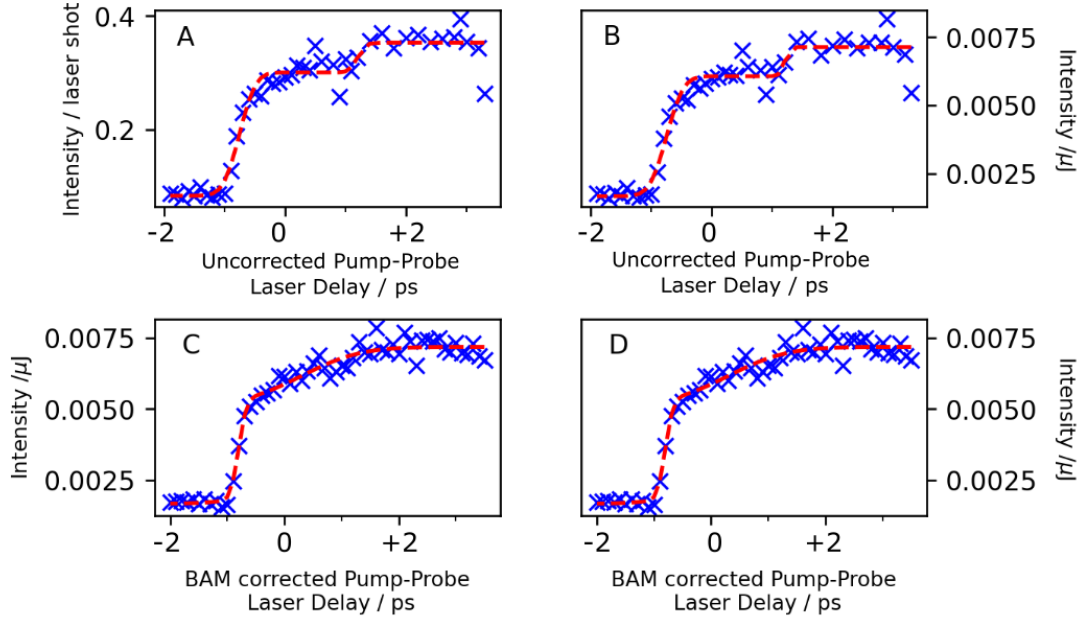


Figure 2.9: Panels A through D show the evolution of the delay-dependent yield of Channel II S^{3+} ions at different stages of correction through the FLASH DAQ. See text for more details.

with a streak camera delay outside one standard deviation from the mean removed. This has not had a noticeable effect on the ion yield, however, there were few laser shots where the streak camera value was markedly different from the average value.

2.5 The PImMS Camera

The Pixel Imaging Mass Spectrometry (PImMS) camera [49, 50, 114–118] provides the ion images that have been used throughout this thesis. The PImMS camera is a time-stamping device that can record the x - and y - spatial position and the time-of-flight, t of an ion event.

The PImMS sensor, that provides the architecture to record these data, comprises an array of independent pixels (PImMS2: 324×324 , used throughout this thesis) mounted inside a camera housing. The camera housing has a camera lens (Nikon Micro NIKKOR 55 mm S-mount macro lens (f/2.8)) to focus light emitted from a phosphor screen onto the pixel sensor array. The PImMS2 camera used throughout this thesis employs a microlens[119, 120] in front of the pixel array. This has

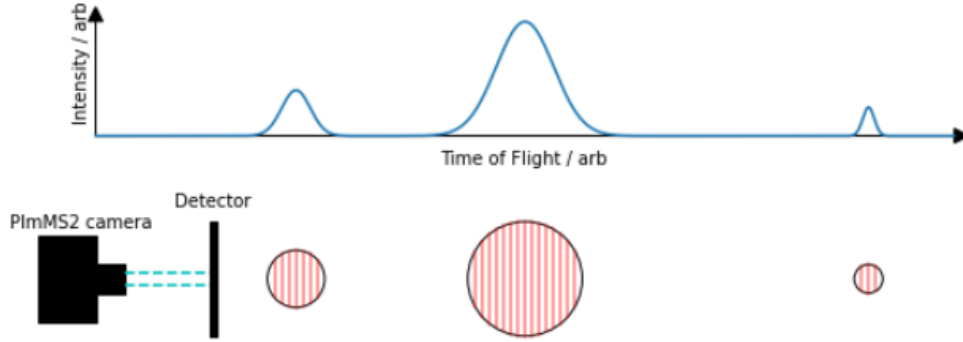


Figure 2.10: The principle of multi-mass imaging experiments is illustrated pictorially. An event-triggered time-stamping device such as the PImMS2 camera records an ion image for each ToF peak.

the effect of focussing light directly onto individual pixels, greatly increasing the sensitivity of the sensor.

The PImMS2 camera is integrated with a LabVIEW interface to record ion events as binary files in the format x, y, t, s , where x, y correspond to the pixel, t corresponds to the flight time, and s corresponds to the acquisition number.

A full explanation of the complicated electronics that comprise each pixel in the sensor is beyond the scope of this thesis and has been discussed in detail in, for example, References [48, 115]. Briefly, each pixel consists of four photodiodes. As a photon impacts upon a pixel, charge accumulates at the photodiodes which generates a small voltage. This voltage is amplified and once surpasses a pixel-dependent threshold voltage, a signal is sent to a digital controller which records the event time-stamp, with a 25 ns timing precision. Each pixel contains four memory registers and can therefore record a maximum of four events per acquisition.

As each pixel is event-triggered, the PImMS2 camera is capable of recording the entire three-dimensional velocity distribution for each ion in the time-of-flight (ToF) spectrum to be recorded, to a timing precision of 25 ns (timebin). This has a number of advantages. Firstly, multi-mass imaging greatly reduces the duration of an experiment, especially for those that produce many ions of interest. In conventional VMI experiments, one would have to repeat the experiment in

order to record another ion. In multi-mass imaging, all ion images are recorded in each acquisition. This has the added benefit of eliminating unaccounted for experimental drift between experiments as all ion images can be recorded under identical conditions. In this way, studies of systems with no prior knowledge of the resultant fragmentation can be performed. The principle of multi-mass imaging is demonstrated in Figure 2.10. A VMI image is recorded for each ToF peak in the acquisition. A further consequence of recording multi-mass ion events during the same acquisition cycle is that ion correlations can be calculated using covariance analysis. This will be discussed in more detail in Section 5.4.2.

2.5.1 Cluster Analysis

Ion events typically illuminate a cluster of pixels, across multiple timebins. Pixels at the centre of a ion cluster are subject to a higher photon flux and therefore typically reach the threshold voltage at earlier timecodes. Therefore the earliest timecodes represent the most accurate timing information for that ion event. Events in adjacent pixels and later timebins correspond to the same ion event. To account for this, ion events corresponding to a cluster of illuminated pixels are identified through a three-dimensional nearest neighbour search and centroided in time and space, using a minimum cluster size and maximum time window for an ion cluster[70, 71, 118, 121]. Through cluster analysis, a single accurate position and time for each ion event can be determined. This algorithm also eradicates ‘noisy’ pixel events that may be triggered randomly and not as a result of an ion event.

Centroiding Algorithm

This section outlines the centroiding algorithm that has been developed previously [70, 71, 122] and is used to identify PImMS ion events to a single pixel position, (x, y) and an accurate arrival-time, t . Firstly, (x, y, t) pixel events that fall within a given time and space window are found and subsequently centroided using the following algorithm:

- 1) The earliest time code in the cluster, t_0 , is taken as the arrival-time of the ion

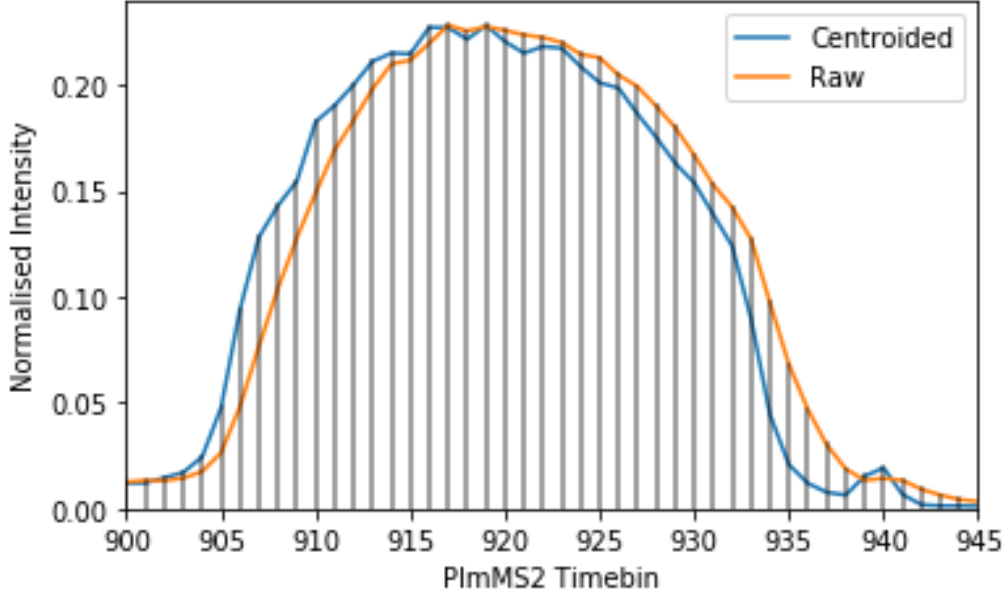


Figure 2.11: Respective ToF profiles before and after centroiding. The centroided ToF profile is shifted toward early ToFs as only the earliest ToF of each ion event is included. This results in the identification of a secondary peak at longer ToFs that would otherwise be unresolved. See text for details.

- 2) Each pixel in the cluster is assigned a weighting, w_i :

$$w_i = \frac{1}{t_i - t_0 + 1} \quad (2.5)$$

- 3) The centroided ion coordinate is calculated based on the weighted average of each pixel in the cluster and its weighting:

$$c(x, y) = \left(\frac{1}{W} \sum_{i=1}^N x_i w_i, \frac{1}{W} \sum_{i=1}^N y_i w_i \right) \quad (2.6)$$

where x_i, y_i are the coordinates of each pixel in the cluster, and W is the total weight of the cluster:

$$W = \sum_{i=1}^N w_i \quad (2.7)$$

Figure 2.11 shows the improvements that centroiding has on the ToF profile for CO^+ ions produced from the one-colour UV photolysis of OCS (imaged under PEISI conditions). The centroided profile (blue) is shifted to earlier ToFs relative to the raw profile (orange). This is a result of each ion event being restricted to a single timebin

and therefore not extending through later timebins. A further consequence of this is the enhanced resolution of a second photofragment centred at PImMS timebin 940. This peak is less resolved in the ToF profile from the raw data as a result of late arriving clusters from the main peak extending into the second ToF range.

Figure 2.12 illustrates the effect that centroiding has on the crushed images of the peaks in the ToF profiles shown in Figure 2.11. The raw crushed image is shown on the left, and the centroided image is shown on the right. The centroided crushed image is less blurred than the raw image and has a greater resolution.

2.5.2 Image Analysis

In conventional VMI experiments, the three-dimensional Newton sphere of photoions is recorded by a two-dimensional particle detector as a series of spatial coordinates integrated along the ToF axis. That is, the two-dimensional projection of the full three-dimensional velocity distribution is recorded. In order to extract kinetic energy and angular distributions, the three-dimensional velocity distribution is required. These are essential for accurate image analysis to be performed.

Under cylindrical symmetrical conditions (as is often the case in VMI experiments), the desired three-dimensional velocity distribution can be fully described by an infinitesimally thin central slice. As PImMS is capable of recording ion images through the Newton sphere, it is possible to measure this slice directly. Chapter 3 will explore methods that achieve this using conventional VMI and also present a new experimental configuration allowing for sliced or three-dimensional velocity imaging with high velocity resolution along the time-of-flight axis.

Inverse Abel Transform

Under cylindrically symmetric conditions, the extraction of the desired three-dimensional velocity distribution from its two-dimensional projection represents a well-known mathematical problem[123], namely the Inverse Abel Transform. If $P(x, z)$ is the (experimentally measured) two-dimensional projection of the three-dimensional distribution $I(r, z)$ on the detector plane (x, z) , then the two are

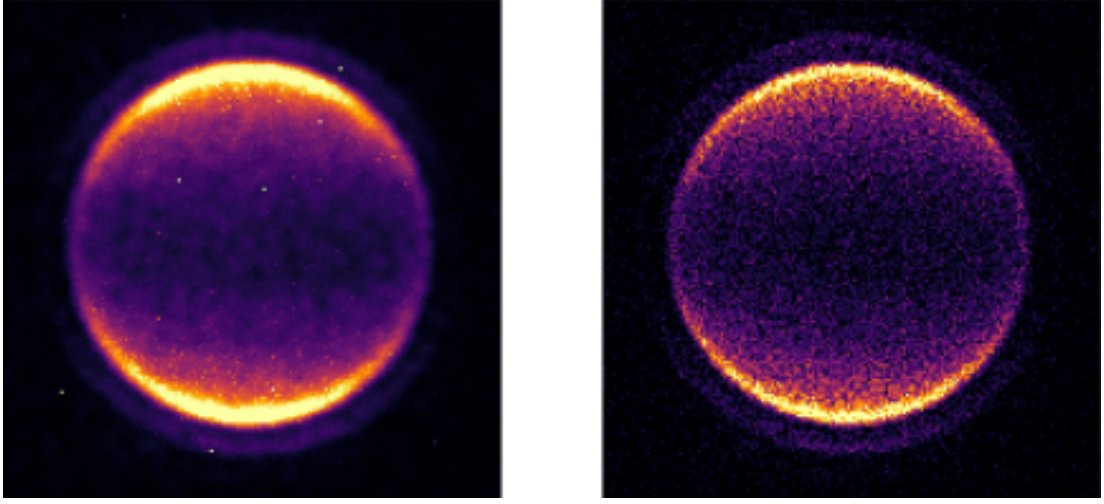


Figure 2.12: Effect of centroiding on the crushed ion image compared to the raw image. The raw image (left) is more poorly resolved than the analogous image obtained from the centroided data (right).

related *via* the Abel integral:

$$P(x, z) = 2 \int_{|x|}^{\infty} \frac{rI(r, z)}{\sqrt{r^2 - x^2}} dr \quad (2.8)$$

The three-dimensional distribution, $I(r, z)$ can theoretically be calculated directly[123]:

$$I(r, z) = -\frac{1}{\pi} \int_r^{\infty} \frac{dP(x, z)}{dx} \frac{dx}{\sqrt{x^2 - r^2}} \quad (2.9)$$

Unfortunately, it is numerically impractical to calculate directly. Instead, numerous algorithms have been developed to approach the problem[124, 125], including the Fourier-Hankel transform[126], onion-peeling[127], BASEX[128], and pBASEX[129] methods.

Throughout this thesis, all inverse Abel transforms have been performed using the pBASEX method[129]. This algorithm is based on the BASEX algorithm in polar coordinates, whereby the angular ion distributions are expanded as a set of Legendre polynomials, and Gaussian functions model the energy distribution. These approximations lead to:

$$I(r, z) = \sum_{k=0}^{k=k_{\max}} \sum_{l=0}^{l=l_{\max}} c_{kl} f_{kl}(R, \theta) \quad (2.10)$$

where

$$f_{kl}(R, \theta) = \exp\left(\frac{(R - R_k)^2}{\sigma}\right) P_l(\cos \theta) \quad (2.11)$$

where c_{kl} are the relative weightings, θ is the relative angle between ion event and the polarisation vector of the photolysis light, P_l is the ordinary Legendre polynomial of order l , R_k is the centre of the k^{th} Gaussian, and σ is the width of the Gaussian functions. This algorithm has been chosen due to its high performance and the accumulation of noise towards the centre of the inverted images which is typically not the region of interest in VMI images.

2.6 Summary

In summary, a detailed discussion of the experimental principles and apparatuses used in this thesis has been given in this Chapter. A description of the processing of PImMS images has also been given. These will be used throughout this thesis. In the following chapter, a novel experimental VMI configuration is presented for enhanced 3D imaging in conjunction with the PImMS camera. This technique is demonstrated in the one-colour photodissociation of OCS using the Oxford VMI spectrometer.

3

Post Extraction Inversion Slice Imaging

This Chapter presents a new experimental configuration for velocity map imaging and demonstrates its applicability to 3D imaging in conjunction with event-based time-stamping cameras, such as the PImMS2 camera. The novel technique, termed Post Extraction Inversion Slice Imaging, is built upon previous existing imaging techniques and can achieve an improved performance in terms of slicing and velocity resolution and three-dimensional imaging capabilities. The underlying concept of PEISI will be explored and discussed and *in silico* development detailed. The imaging technique will subsequently be benchmarked against other imaging techniques by recording the full three-dimensional velocity distribution of photofragments following the UV photodissociation of carbonyl sulfide at around 230 nm.

3.1 VMI Techniques

Since the development of velocity map imaging[44], many techniques have been added or applied to build upon the powerful tool. In ‘crushed’ imaging, the two-dimensional projection of the full three-dimensional Newton sphere of ions is recorded. If the Newton sphere possesses an axis of cylindrical symmetry between the detector plane and the polarisation of the photolysis laser, then the full three-dimensional velocity distribution can be mathematically reconstructed through

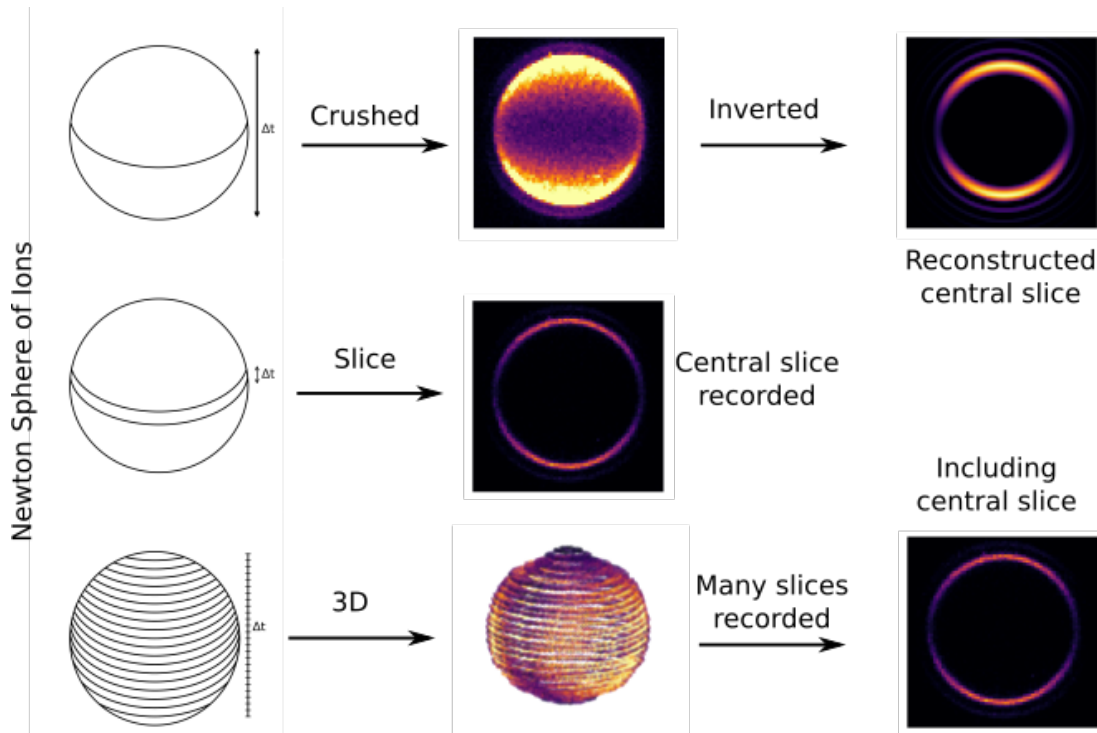


Figure 3.1: The three methods commonly employed in Velocity Map Imaging experiments and corresponding images that are typically extracted. Image shown is the CO^+ photofragment following the UV photodissociation of OCS.

algorithms based on the inverse Abel transform[123]. These algorithms aim to return an infinitesimally thin slice in the image plane, from which (for cylindrical symmetric distributions) the full three-dimensional velocity distribution can be retrieved[126–130]. Unfortunately, these algorithms do have their drawbacks. In order to validly reconstruct the central slice, the whole velocity distribution must be recorded. This can be troublesome for images with both fast and slow features as the slow features necessarily have poorer velocity resolutions. Also, these algorithms can introduce artefacts into the reconstructed image. This is especially true of images that contain a lot of noise. Changes to the input parameters of these algorithms can help to improve the quality of the reconstruction but this is not guaranteed. The concept and images procured from ‘crushed’ imaging are illustrated in Figure 3.1.

In attempts to bypass the sometimes strict pre-requisites of these algorithms, ‘slice’ imaging was developed by Kitsopoulos *et al.*[131]. As alluded to, the entire three-dimensional velocity distribution of cylindrically symmetric data can be

determined from the central slice of the Newton sphere in the image plane. In slice imaging, the central slice of the Newton sphere is directly recorded and thus describes the full velocity distribution. This is usually done by expanding the Newton sphere as much as feasibly possible. The extraction field is switched on after a post-ionisation extraction delay, τ . The nascent Newton sphere is allowed to expand in field-free conditions for typically around 250 ns before the field is rapidly switched on. This has the effect of a larger ion arrival time spread at the detector. By gating the detector to a suitable narrow time width (<40 ns) a central sliced portion of the expanding Newton sphere can be recorded. This is illustrated in the Figure 3.1.

The most common approach to slicing is known as ‘DC-sliced’ imaging, developed independently by Townsend *et al.*[132] and Lin *et al.*[133]. This technique introduces a third electrostatic plate into the apparatus. This allows a smaller potential difference to be employed in the interaction region while retaining velocity mapping conditions. This is crucial as it allows ions initially travelling anti-parallel to the time-of-flight (ToF) axis longer to turn around and begin travelling toward the detector. This extra time has the effect of stretching out the Newton sphere of ions at the detector resulting in a longer time-of-arrival spread and a thinner central slice is achievable.

Full three-dimensional velocity map imaging became a possibility with the advent of complementary metal oxide semiconductor (CMOS) technology[48]. Previously, technology had restricted this method to experiments with very low count rates using delay line anodes[45, 46, 134, 135]. Unfortunately, these are not feasible for typical ion imaging experiments with ion counts $> 10 \text{ shot}^{-1}$. Event-based pixel sensors such as Pixel Imaging Mass Spectrometry[48, 136, 137] (PImMS) and Timepix[51, 53] consist of an array of pixels each of which acts as a clock. These sensors allow for ions of different masses to be recorded during the same acquisition[137] and by extension, slices of a single Newton sphere of ions may be imaged as the ion cloud arrives at the detector. The three-dimensional imaging of an expanding Newton sphere is displayed in the bottom row of Figure 3.1. Each

timebin records a separate image of which one will contain the central slice of the Newton sphere akin to that recorded in slice imaging.

3D imaging was demonstrated by Amini *et al.*[118] using the PImMS1 camera to image the Newton sphere of CO and S photofragments following the UV photodissociation and subsequent Resonance-enhanced multiphoton ionisation (REMPI) of OCS in a DC-slicing set-up. Up to 12 slices through the Newton sphere were obtained. As PImMS records the full three-dimensional distribution as the ion cloud arrives at the detector, an equivalent ‘crushed’ image can be extracted by integrating the ion image over the entire ToF peak. A velocity resolution of 0.06 was attained from the central slice image for the CO($J = 46$) photofragment, limited by the pixel array of PImMS[118].

However, as DC-slicing is a technique designed for instruments that are only capable of recording a ‘crushed’ or ‘central slice’ image it seems reasonable that the technique may not be the most suitable for a camera such as PImMS or Timepix3. In this respect, a new technique was sought that better utilised the 3D imaging capabilities of these cameras.

3.2 Post Extraction Inversion Slice Imaging

The 3D imaging capability of PImMS and similar sensors is utilised most effectively by increasing the time spread over which ions arrive at the detector. This means that the ions arrive over a greater number of PImMS timebins and hence more slice images of the Newton sphere may be recorded. This is also the objective in ‘slice’ imaging[131] and is achieved by decreasing the extraction voltages. This has three drawbacks. Firstly, although decreasing the extraction voltages does increase the temporal spread of the Newton sphere it also has the effect of increasing the extent of the Newton sphere. Thus this determines the absolute limit on the minimum working voltages, as below a certain voltage the desired part of the Newton sphere will become too extended and will not impinge on the detector. The minimum value of this threshold depends on the initial velocity of photofragments and the dimensions of the spectrometer and detector. Secondly, ions accelerated in a lower

extraction field will gain less kinetic energy than at higher voltages. The detection efficiency of ions is highly dependent on the corresponding kinetic energy as they impinge on the detector[138, 139]. Therefore, if the extraction field is too low then ions may not be detected at all which is obviously an impractical setting. Thirdly, in low extraction fields nascent ions are highly susceptible to stray fields that can be very difficult to isolate and subsequently eradicate. At the lowest extraction voltages, the magnitude of stray fields may be comparable to the VMI field and thus cause relatively large distortions that may significantly effect the ion trajectories. This effect will be amplified as stray fields are rarely homogeneous and will therefore affect ions differently depending on their inception. In ‘slice’ imaging, ions expanding in field-free conditions are particularly vulnerable to distortion effects as there is no field to guide them onto the detector.

Any imaging technique must go some way to eradicating these issues while still increasing the ion arrival time.

3.2.1 Concept

The development of a new ion optic set-up that increases the ion arrival time was developed based on the Post-Extraction Differential Acceleration (PEDA) technique used in mass spectrometry first introduced by Aoki *et al.*[140]. Aoki *et al.* developed the method to account for the large dispersion in the velocity distribution of nascent ions, inherent to matrix-assisted laser desorption ionisation (MALDI) in order to increase the mass resolution[141]. In such experiments, electric fields are used to extract ions in a similar way to velocity map imaging. However, the field is chosen such that ions are spatially focussed at the detector. The spread of velocities of ions causes temporal overlap at the detector of ions with different mass-to-charge ratios and distinct ions become unresolvable.

PEDA overcomes this by applying an increased voltage to the extraction electrode at a time delay, τ , post-extraction. This extra voltage affects the kinetic energy gained by ions depending on their position along the ToF axis at time, τ . With the

properly selected time delay, τ_0 , ions within an optimised mass-to-charge ratio, m/z , range are focussed temporally at the detector, thus improving the mass resolution.

The ultimate goal of PEDDA is to reduce the arrival time spread of ions of a given mass-to-charge ratio, *i.e.* to ‘pancake’ the Newton sphere onto the detector. This is the opposite aim of the ion optic development that is sought here. However, by slightly altering the set-up, the PEDDA pulse can be manipulated to achieve an increase in ion arrival time.

A new ion optic set-up was developed with the introduction of two new plates to a DC- slicing ion optic arrangement – one of which is to be pulsed post-extraction and the other grounded. Ions are extracted and the Newton sphere expands along the ToF axis through the repeller, extractor, and third lens plates. At a time delay, t_P , a voltage is applied to the pulsed plate of the ion optic arrangement. This causes an acceleration in the the Newton sphere of ions: ‘slow’ ions at the back (along the ToF axis) of the Newton sphere are accelerated the most and ‘fast’ ions at the front of the distribution the least. This is due to:

$$\Delta E_k = qV_P \left(1 - \frac{\Delta x}{L}\right) \quad (3.1)$$

where ΔE_k is the kinetic energy gained by an ion in the pulsed region, V_P is the pulsed voltage, Δx is the relative distance on the ToF axis between the ion at t_P and the pulsed plate, and L is the distance between the pulsed plate and the grounded plate further along the ToF axis (after which ions experience no force).

Ions leave the pulsed region and travel at a constant speed, v_{FF} in the field-free region, given by:

$$v_{FF} = \sqrt{\left[v^2 + \frac{2qV_P}{mL} \left(1 - \frac{\Delta x}{L}\right)\right]} \quad (3.2)$$

where m and q are the mass and charge of the particle, and v is the velocity component in the ToF direction for a given ion in the pulsed region, and varies slightly with the initial velocity. If V_P is suitably large and t_P is chosen properly, then the second term dominates this equation. The longest ion arrival time spread

occurs for a pulsed time, t_P , such that ‘fastest’ ions are just leaving the pulsed region and entering the field-free region. This means that $\Delta x_{\text{‘fastest’}} = L$ and:

$$v_{\text{FF,‘fastest’}} = v_{\text{‘fastest’}} \quad (3.3)$$

while the other ions have velocity:

$$v_{\text{FF}} = \sqrt{\left(v_P^2 + \frac{2q\Delta x(v)V_P}{mL}\right)} \quad (3.4)$$

where, v_P is the ion velocity at the pulsed time, t_P , $\Delta x(v)$ is the distance between the ion and the second grounded plate at the pulsed time, t_P , and depends on the initial velocity component in the ToF direction, the ion optic configuration, and the extraction fields. Ultimately, the ‘slowest’ ions leave the pulsed region with the largest velocity.

In the field-free region, ions will ‘pancake’ as they come into temporal focus at some point in the flight tube. At this point, all ions have roughly the same position on the ToF axis. After this point, the ‘slow’ ions overtake the ‘fast’ ions and a Newton sphere inversion occurs and the Newton sphere is temporally defocussed along the ToF axis. Ions arrive at the detector over a much longer arrival time and the Newton sphere can be imaged across many more PImMS timebins.

The general PEISI scheme is shown in Figure 3.2, where ions with a range of velocities in the ToF direction are accelerated according to a PEISI field in the Oxford spectrometer. The ToF position of each ion is plotted as a function of its time-of-flight as ions pass through successive electric fields. Here, the Oxford spectrometer has been simulated simply along the ToF axis with ions modelled as point charges through a series of changing electric fields. Ions initially travelling in the positive and negative ToF direction are coloured blue and green, respectively. The ‘fast’ ions (blue) remain further along the ToF axis than the others initially. The first horizontal line, at ≈ 0.1 m, represents the pulsed plate. Once the ‘fast’ ions reach the second horizontal line, representing the start of the field-free region, the pulsed field is switched on. All ions experience an additional force and are differentially accelerated. Once all ions have passed through the second horizontal

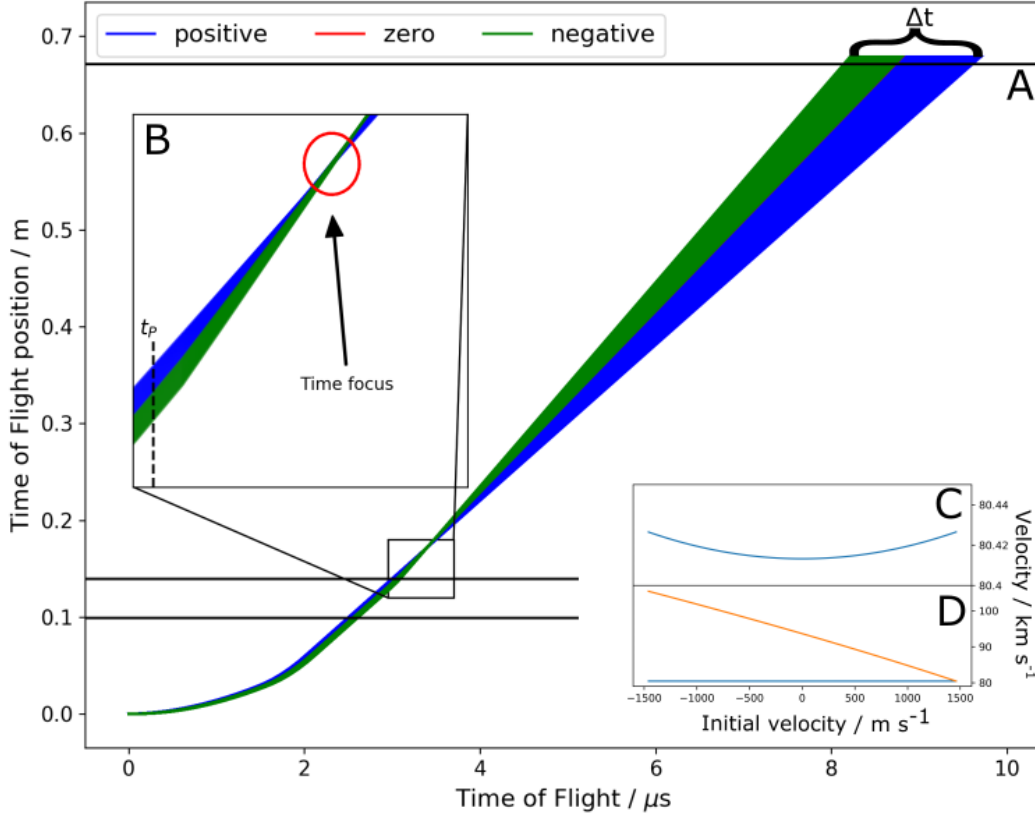


Figure 3.2: A) Ion trajectories in PEISI with varying initial velocities. The ToF position of each ion is plotted as a function of its time-of-flight. Blue and green corresponds to ions with an initially positive or negative ToF velocity. B) Zoom plot of trajectories around t_p , the temporal focus of ions is circled. C) The velocity of ions at t_p . D) Comparison of the velocities shown in C (blue) and the corresponding velocity of ions as they leave the pulsed region (orange). Ion arrival time, Δt is marked at the detector. See text for more details.

line, they cease to experience a force and travel at constant speed to the detector. The velocity differential between the ‘front’ and ‘back’ of the Newton sphere is significant. Shortly after this time, the ions reach temporal focus after which they are defocussed. This can be seen at the third horizontal line, at $\approx 0.68\text{ m}$, representing the detector, the ion arrival time, Δt , is $\approx 1.5\text{ }\mu\text{s}$. This compares to an ion arrival time, Δt of $0.1\text{ }\mu\text{s}$ with no PEISI pulse. The Newton sphere can now be sliced with high resolution along the ToF axis using a conventional detector or a timestamping camera such as PImMS2.

Panel B zooms in on the ion trajectories around t_p , shown as a vertical dashed line. After this time, ions are differentially accelerated. This can be seen as the

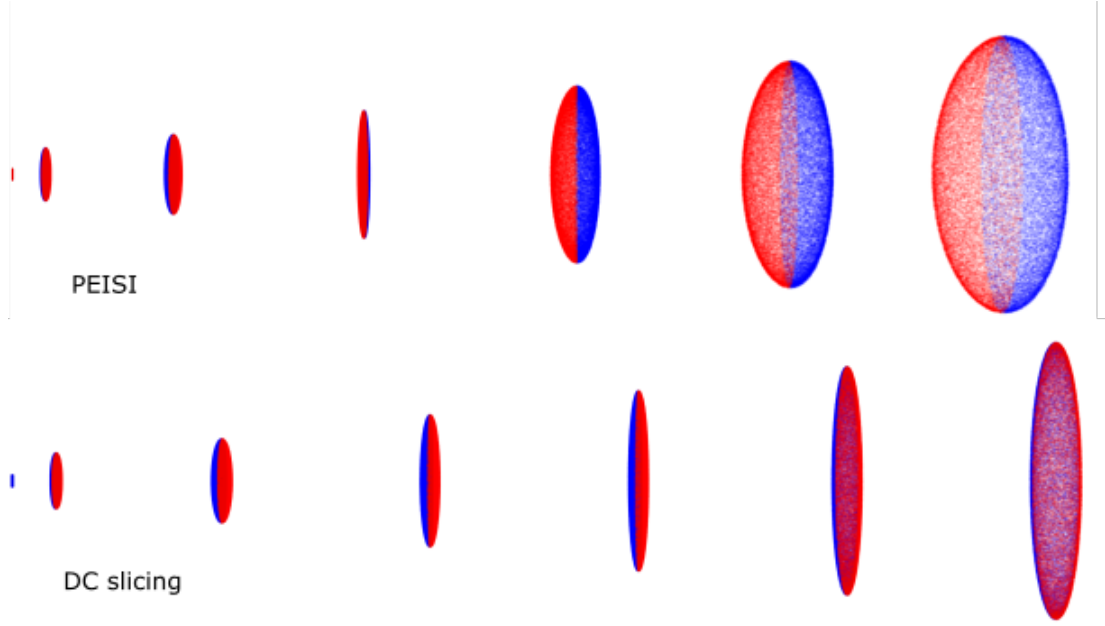


Figure 3.3: Simulated ion trajectories of CO^+ photofragments with 0.3 kV kinetic energy under PEISI and DC slicing conditions. Ions with an initially negative velocity component in the ToF axis are shown in blue and positive in red. Each Newton sphere is shown in $1.25\mu\text{s}$ increments.

‘slow’ ions come closer to the blue ions. The gradient of the ‘fastest’ ions (left most blue markers) remain constant as they are not accelerated. In the red circle, Newton sphere ‘pancaking’ occurs where all ions have roughly the same position on the ToF axis and are temporally focussed.

Panel C shows the velocity of ions in the pulsed region before t_p as a function of initial velocity and varies a little but is negligible with a sufficiently large PEISI pulse. This is illustrated in Panel D which compares the velocities shown in Panel C with the velocities of ions leaving the pulsed region.

As the PEISI pulse creates an electric field along only the ToF axis, only the ToF-component of the velocities of ions are affected. This increases the ToF velocity component significantly thus reducing the overall ToF. An implication of this is that the extent of the Newton sphere in the detector plane is decreased as the transverse velocities have less time to expand toward the edge of the detector.

A simulated comparison of CO^+ photofragments borne with a kinetic energy of 0.3 keV in DC-slicing and PEISI conditions is shown in Figure 3.3. The Newton

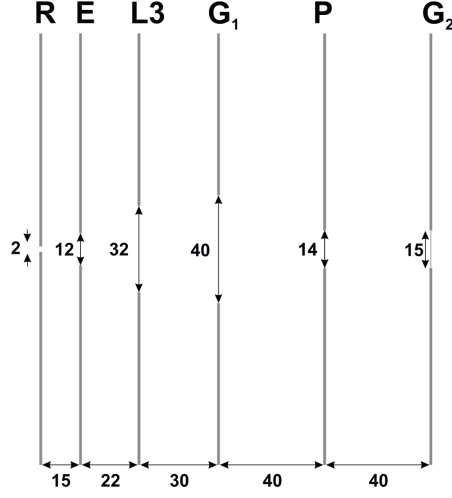


Figure 3.4: Schematic of the ion optic configurations employed for Post Extraction Inversion Slice Imaging. R, E, L3, G_i , P correspond to the repeller, extractor, third lens, grounded plates, and pulsed electrodes, respectively. All measurements are given in mm. Figure adapted from Reference [90].

sphere of ions is plotted at a constant time step. Both simulations were performed with a repeller voltage of 1 kV and a repeller, extractor, third lens ratio of 1 : 0.886 : 0.75. The pulsed voltage, V_P under PEISI conditions was set at 3 kV at an optimised switch time, t_P of $2.9 \mu\text{s}$. Each simulation comprised 50,000 trajectories. In each simulation, ions borne with a positive (negative) velocity component in the ToF direction are shown in red (blue). The ‘pancaking’ and subsequent Newton sphere ‘inversion’ under PEISI conditions are apparent in the third and fourth plot.

3.2.2 Ion Optic Configuration

The ion optic geometry configuration was optimised through extensive ion trajectory simulations[90] using the Simion 8.0[142] software.

Genetic Algorithm

As the problem involves multi-dimensional variables (the voltages on each of the plates, the geometries of each of the plates, the aperture size of each of the plates, and the switch time), a brute force approach to the optimisation was too computationally inefficient. Instead, a genetic algorithm approach was employed that directly communicates with the Simion software.

The genetic algorithm aims to maximise the time spread of an ion Newton sphere as it arrives at the detector, while maintaining velocity mapping conditions. In good velocity mapping conditions, it is assumed that there is a linear relationship between the radius at which an ion strikes the detector and the initial speed in the detector plane of the ion. It is also assumed that there is a linear relationship between the ion time-of-flight and the initial velocity in the time-of-flight direction. Both of these measures can be quantified by R^2 , the square of the Pearson correlation coefficient, r .

$$R^2 = r^2 \quad (3.5)$$

The Pearson correlation coefficient, r , of a sample may be defines as:

$$r = \frac{\sum(x_i y_i - n \bar{x} \bar{y})}{(n-1)s_x s_y} \quad (3.6)$$

where x_i and y_i are the measure values for the two variables x and y , $\bar{x}$ and $\bar{y}$ are the means of x and y , n is the number of values in the sample, and s_i are the sample standard deviations of the two variables.

R_{xy}^2 and R_{ToF}^2 are the R^2 values that correspond to the velocity mapping in the planar and in the time-of-flight direction. The time spread of an ion Newton sphere, Δt , refers to the difference between the earliest and latest ion times-of-flight.

The genetic algorithm functions as follows:

- **Initialisation:** A series of sets of parameters is generated where the value of each parameter is restrained to within an experimentally viable range. The whole series is known as the ‘population’ and an individual set is known as a ‘member’ of the overall population.
- **Fitness Evaluation:** For each member of the population, a number of ions are flown under those experimental conditions. The R^2 values and Δt are calculated. From this a ‘fitness’ for each member is calculated, representing how optimal the member is for the PEISI experiment.

- **Tournament Selection:** This section chooses ‘parents’ that are to be added to a ‘breeding pool’. Small sections of the populations are randomly generated, termed ‘tournaments’. Within each ‘tournament’, the member with the best fitness is declared the winner, and this member is added to a ‘breeding pool’, from which the next generation will be formed. Tournament selection continues until the breeding pool is the same size as the population.
- **Crossover:** Two parents from the breeding pool are selected and a child is generated from them by randomly selecting a value for each variable between the the value of its parents. This ‘crossover’ process is repeated until a new generation is completed. By crossing over the successful members of the tournaments, the algorithm will converge on the configuration with the best fitness.
- **Mutation:** For each new parameter that a child receives from its parents, there is a probability that a ‘mutation’ occurs and that parameter is randomly generated. Mutations are intended to ensure that the genetic algorithm explores a large area of the problem space and does not converge on a local maxima but finds the global maxima.
- **Repeat:** Now the population of the next generation is fully generated, the fitness of the new generation is evaluated and the process repeats. The algorithm can be repeated for a set number of generations or until a threshold value of the metric has been achieved.

The genetic algorithm was repeated for a range of ions with mass-to-charges and initial kinetic energies of ions to ensure its application to a wide range of scenarios. The PEISI optimised ion optic configuration is shown schematically in Figure 3.4. The pulsed plate is an open electrode and the second grounded plate includes a thin mesh grid which removes grid distortion effects in the images, but decreases ion transmission. Simulations were performed with and without a pulse width for the rise time (50 ns) of the pulsed voltage to ensure no distortions

were introduced to the velocity mapping of ions and showed that there were no detrimental effects. Although, these simulations have been performed specifically for the Oxford VMI Spectrometer, there is no reason that this method could be applied to spectrometers of smaller or larger MCP detectors.

3.3 Simulations

3.3.1 3D slice images

The 3D slice imaging capabilities were simulated for CO photofragments with an initial kinetic energy of 0.3 keV — a typical kinetic energy release for such photofragments following photodissociation. Simulations of both DC-slicing and PEISI were performed for comparison. The repeller voltage was set at 1 kV in the voltage ratio mentioned above. A pulsed voltage of 3 kV was applied at a time, t_P , of $2.9 \mu\text{s}$ post-extraction for PEISI. The final detector coordinates were converted into PImMS measurements. Times-of-flight were blurred with a Gaussian convolution ($\text{FWHM} = 25 \text{ ns}$) to simulate the timing resolution and subsequently binned into 25 ns timebins to simulate the timing precision of PImMS. The (x, y) coordinates were converted to pixels using experimentally determined relations between detector dimensions and PImMS pixels.

The results of the simulated slice images arising from DC slicing and PEISI conditions are shown in Figure 3.5. Panels a) and b) show simulated images of the first half of the Newton sphere arriving at the detector under PEISI and DC slicing conditions, respectively. Simulated images are nearly symmetric around the central slice and are therefore not included.

From these simulated images, a number of features of PEISI alluded to can already be seen. Firstly, the increase in ion arrival time is apparent from the number of PImMS timebins that comprise the image. At a relatively high extraction voltage ($V_R = 1 \text{ kV}$), a factor of four increase in the number of PImMS timebins is observed. Secondly, the central slice images of the Newton sphere recorded under both PEISI and DC slicing conditions (labelled timebins 12 and 3, respectively) are very sharp. The central slice recorded under DC slicing conditions displays a

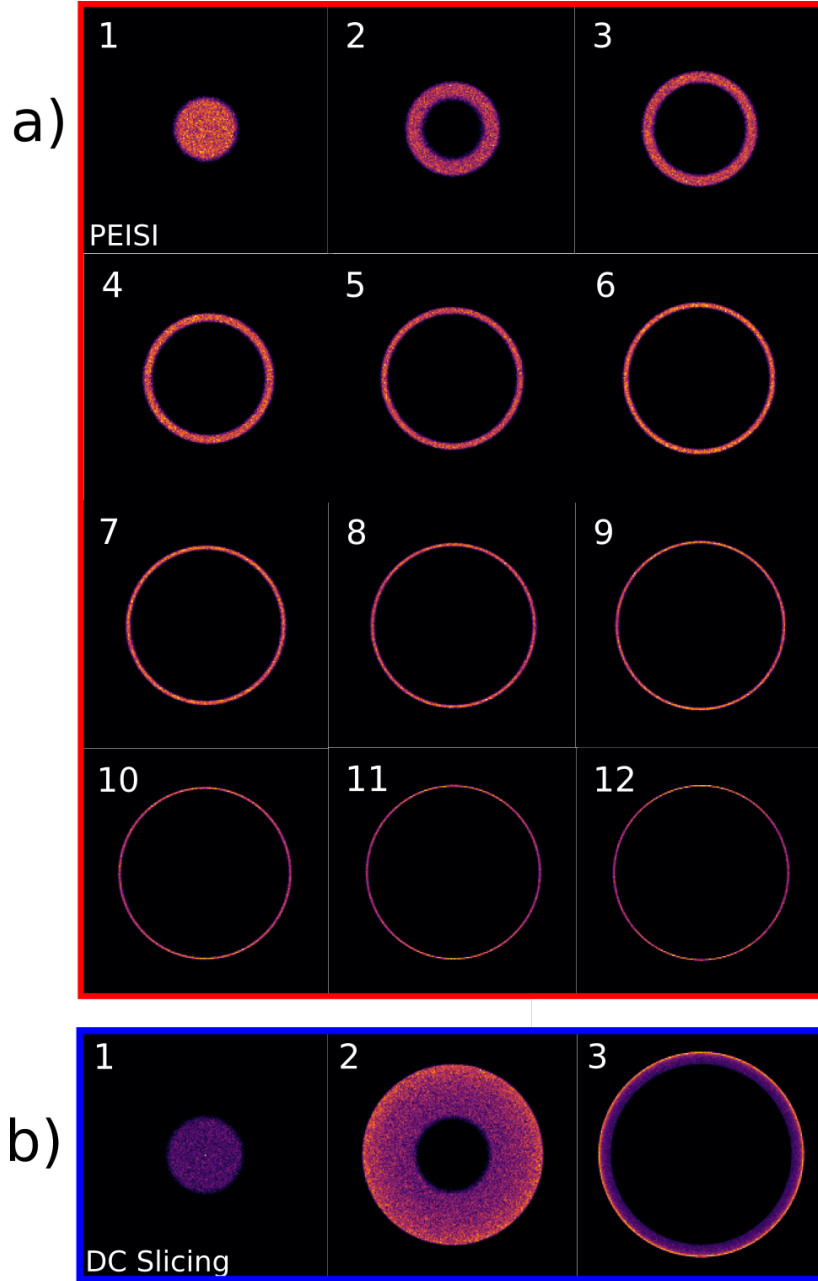


Figure 3.5: Simulated VMI images of CO ions in the Oxford Spectrometer recorded with a PImMS2 camera with a repeller voltage of 1 kV. Panel a) shows the simulated images recorded under PEISI conditions ($V_P=3\text{ kV}$); and panel b) under DC slicing conditions. The relative timebin is shown for each image. Ion images only up to the central slice are included for brevity as images are nearly symmetric about the central slice.

slight blurring at lower radii due to out-of-plane contributions. The non-central slice image recorded under DC slicing conditions (timebin 2) suffers greatly as the out-of-plane contributions become increasingly significant. Under PEISI conditions, the time for the Newton sphere to arrive at the detector completely is much longer, and so a relatively thin slice of the Newton sphere arrives during a single timebin. In fact, only in the first three timebins do the slices images suffer an appreciable decrease in velocity resolution.

3.3.2 Time-of-Flight Profile

The shape of the time-of-flight profile arising from ions arriving at the detector under PEISI conditions depends on a variety of factors. These factors may affect the total ion arrival time at the detector or the shape of the intensity profile or both.

The magnitude of the extraction electric field, V_R , the pulsed voltage, V_P , and the mean speed of the nascent ion, $\bar{v}_0$ affect the ion arrival time spread, Δt .

The angular distribution, $P(\theta, \phi)$, of the photoion and the detection efficiency, $\eta(E_{k,f})$, of ions with a given kinetic energy at the detector, $E_{k,f}$ affect the shape of the intensity profile. As the final kinetic energy is dominated by the extraction field, the extraction field can be considered to also affect the shape of the ToF intensity profile.

Figures 3.6, 3.8, and 3.9 investigate the effect of each of these factors on the shape of simulated ToF intensity profiles under PEISI conditions. Each simulation comprised 100,000 CO^+ trajectories under a combination of PEISI conditions, varying the repeller voltage, V_R , the pulsed voltage, V_P , the initial mean speed of CO^+ , $\bar{v}_0$ used for a three-dimensional Gaussian velocity distribution, the anisotropy parameter, β , of the angular distribution of ions assuming the form:

$$P(\theta) = \frac{1}{4\pi} (1 + \beta P_2(\cos \theta)), \quad (3.7)$$

where β is the spatial anisotropy parameter and is defined:

$$\beta = 2 \langle P_2(\cos \theta) \rangle, \quad (3.8)$$

where $P_2(\cos \theta)$ is the second ordinary Legendre polynomial, and θ is the angle between the electric vector of the light and the recoil direction of the photofragment.

V_R / V	V_P / V	$\bar{v}_0 / \text{m s}^{-1}$	β
500	1000	1260	2
1000	3000	1460	-1
3000	5000	1660	0

Table 3.1: Summary of PEISI variables investigated.

The variables used in the simulations are summarised in Table 3.1. The switch time, t_P , used in each simulation has been optimised for the corresponding repeller voltage. The exponential rise time, τ , of the pulsed field, V_P , was assumed to be a constant of 50 ns, the quoted rise time of the electronic switch that is used experimentally. The pulsed voltage, $V(t)$, after the switch time, t_P is given by:

$$V(t) = V_P \left[1 - \exp \left(-\frac{t - t_P}{\tau} \right) \right] \quad (3.9)$$

For the investigation of the effect of each variable, the other variables are kept constant for each simulation while the dependent variable is changed as according to Table 3.1. In each simulation, one variable from Table 3.1 is changed and the other parameters are held constant.

Panel A of Figure 3.6 shows the simulated ToF profiles for ions in DC slicing conditions (equivalent to PEISI conditions with a pulsed voltage, $V_P = 0 \text{ V}$) at different repeller voltages, for reference. As expected, times-of-flight are shorter for ions accelerated by a larger field. The ion arrival time, Δt , also decreases with increasing repeller voltages as ions at the back of the Newton sphere are accelerated to relatively higher velocities and therefore arrive earlier.

Panel B shows the effect that different velocity distributions have on Δt from three simulations. Each simulation was performed with a repeller voltage, $V_R = 1 \text{ kV}$ a pulsed voltage, V_P of 3 kV, and an isotropic angular distribution. The simulations differ by the magnitude of the initial velocity of CO^+ ions, shown in Table 3.1. The shape of the intensity profile remains unchanged as the initial velocity is changed. The ion arrival time spread, Δt , does increase with increasing velocity magnitude. This makes sense as ions trajected anti-parallel to the ToF axis take longer to turn around and begin travelling toward the detector. Therefore, the Newton sphere is

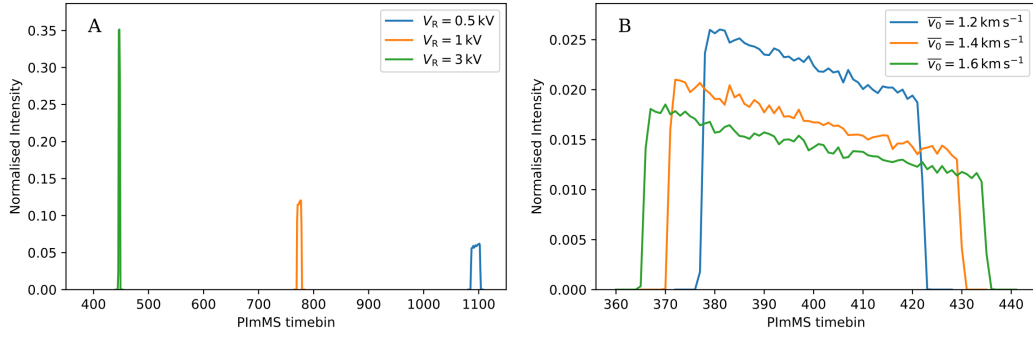


Figure 3.6: Simulated ToF profiles arising from varying the parameters in Table 3.1. Panel A shows the simulated ToF profiles obtained under DC slicing conditions at increasing repeller voltages. Panel B shows the simulated ToF profiles for Newton sphere of ions with varying velocity distributions. See text for full explanation of each panel.

more extended at time t_p when the pulsed field is applied. Thus the ‘slow’ ions gain more kinetic energy and enter the field-free region with a higher velocity than the respective ions from the other two simulations.

Each ToF profile simulated under PEISI conditions in Panel B of Figure 3.6 display a trapezoidal shape to the profile. This effect derives from the velocity mapping of ions along the ToF axis under PEISI conditions. Ions are not linearly mapped onto time-of-flight, as shown in Figure 3.7. There is a quadratic relation between time-of-flight and the initial velocity component in that direction. PImMS timebins have the same temporal size, however, ions of a larger velocity range comprise the earlier bins, resulting in an enhanced intensity.

Panel A of Figure 3.8 shows the effect the extraction voltages have on Δt .

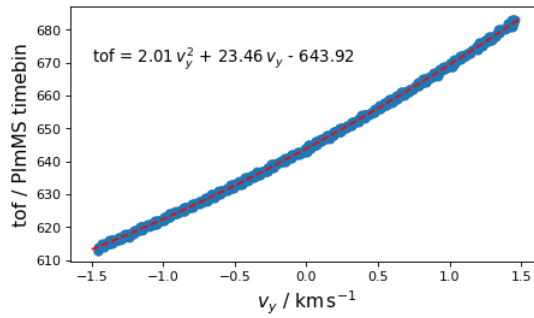


Figure 3.7: Relationship between ToF and initial velocity component in the ToF direction, v_y .

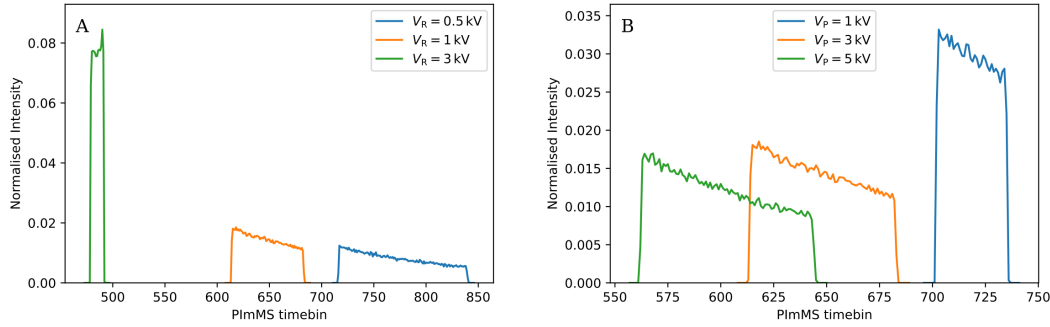


Figure 3.8: Simulated ToF profiles arising from varying the parameters in Table 3.1. Panel A shows the simulated ToF profiles obtained under PEISI conditions with an increasing repeller voltage at a constant pulsed voltage. Panel B shows the simulated ToF profiles obtained with an increasing pulsed voltage at a constant repeller voltage.

Each simulation had the same three-dimensional Gaussian velocity distribution, centred at $\bar{v}_0$, a pulsed extraction voltage, V_P of 3 kV, and an isotropic angular distribution. The ion arrival time spread, Δt , is strongly dependent on the repeller voltage, V_R . By comparing the DC slicing ToF profile in Panel A of Figure 3.6 with the corresponding repeller voltage in Panel A of Figure 3.8, an increase of 8 PImMS timebins to 71 PImMS timebins is observed. Lower repeller voltages, $V_R=500$ V (blue) lead to a longer turn-around time for ions initially travelling in an initially negative ToF direction, in a similar way to the faster ions in a Panel B of Figure 3.6. Thus the Newton sphere is far more extended by the time the PEISI field is applied and therefore a greater velocity differential is observed for ions after they leave the post-extraction region and therefore a larger arrival time spread. Here, an ion arrival time spread corresponding to 125 PImMS timebins is observed. Conversely, ions from the simulation with a higher extraction field, such as 3 kV (green) experience a relatively much greater force, resulting in, first, a shorter turn-around-time and second; a less extended Newton sphere by the time the pulsed voltage is applied to the plate. The distance between a given ion and the pulsed plate, Δx , determines the kinetic energy gained. Therefore, the smaller the distance between the ‘slowest’ and ‘fastest’ ions at time, t_P , the smaller the velocity differential and therefore the smaller ion arrival time spread, Δt .

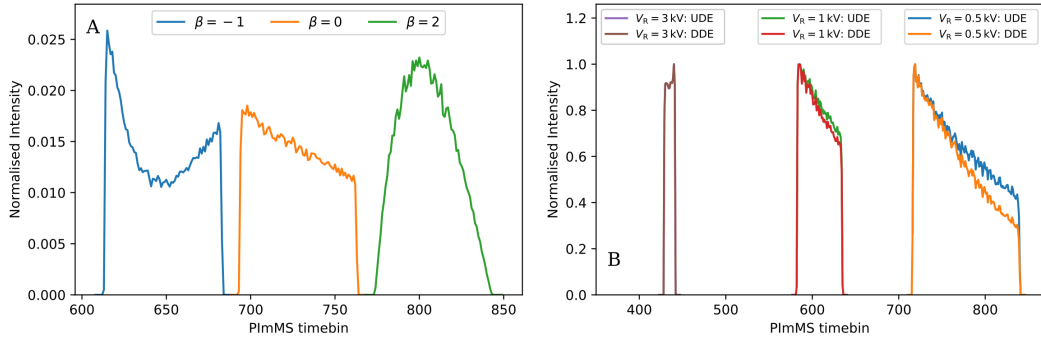


Figure 3.9: Simulated ToF profiles arising from varying the parameters in Table 3.1. Panel A shows the simulated ToF profiles obtained under PEISI conditions of Newton spheres with varying angular distributions. Panel B shows the effect of differential detection efficiency of ions has on the ToF profiles at a range of repeller voltages. Traces labelled UDE indicate a unity detection efficiency of ions and traces labelled DDE indicate a differential detection efficiency based on the kinetic energy of the ions at those times-of-flight. Kinetic energy dependent detection efficiencies were based on Reference [139], see text for more details.

Panel B of Figure 3.8 shows the effect the magnitude of the pulsed voltage, V_P , has on the ion arrival time spread, Δt . The repeller voltage was kept at 1 kV for each simulation with a varying pulsed voltage of 1, 3, and 5 kV applied, respectively. As expected, ion arrival time spread increases with increasing, V_P . Increasing the pulsed voltage from 1 kV, to 3 kV, to 5 kV, increases the number of PImMS timebins that the Newton sphere is recorded in from 35, 71, 83, respectively. In this simulation, the extraction fields were kept constant and therefore equivalent ions have identical positions and velocities at t_P . As long as the ions are between the pulsed plate and the second grounded plate at t_P , the ions are accelerated toward the detector. Therefore, the higher the pulsed voltage, the larger the differential velocity and the longer the time-of-flight arrival spread. As the fast ions are unaffected by the PEISI pulse, its ToF will remain unchanged regardless of the magnitude of V_P , hence the observed increase in PImMS timebins observed.

Panel A of Figure 3.9 shows the effects that a $\sin^2 \theta$ (blue), a $\cos^2 \theta$ (green), and an isotropic (orange) distribution have on the ToF profile under PEISI conditions. For each simulation, constant values of V_R , V_P , and $\bar{v}_0$ were employed and each trajectory therein was subsequently weighted according to Equation (3.7).

If no weighting is added, Simion 8.0 samples trajectories uniformly and therefore returns an isotropic distribution. This case corresponds to a spatial anisotropy parameter, $\beta = 0$ and the ToF profile takes the aforementioned trapezoidal shape. This is confirmed for the simulation of the isotropic distribution (orange). The $\sin^2 \theta$ distribution, corresponding to a spatial anisotropy parameter, $\beta = -1$, has maximal probability values for $\theta \approx \frac{\pi}{2}$. The polar coordinates at the time-of-flight extrema correspond exclusively to such angles and therefore have a cumulative much higher probability in such a distribution. This explains the enhanced intensity at these times-of-flight. The difference in intensity between opposite ends of the Newton sphere is explained on the same grounds as the trapezoidal shape observed previously. At times-of-flight toward the centre of the peak, there is on average a polar angles, θ closer to 0 and π which have minimal values in a $\sin^2 \theta$ distribution. This explains the drop in intensity observed. The intensity is still non-zero, however, because in the central slice frame, trajectories with polar angles other than 0, π exist, which have non-zero probability.

The explanation for the $\cos^2 \theta$ distribution is similar. At the time-of-flight extrema, corresponding to θ values of approximately $\frac{\pi}{2}$, there is a node in the probability distribution hence these are regions of zero intensity. As at these times-of-flight, the polar angle, θ , converges to $\frac{\pi}{2}$, the intensity drops to zero. Away from the extreme times-of-flight, ion trajectories have θ values $\neq \frac{\pi}{2}$ and hence there is always intensity. At timebins toward the central time slice, the average polar angle tend to ≈ 0 and π and thus a larger probability, explaining the maximum in intensity. The reverse process occurs after the central time slice, ultimately ending at zero intensity as the polar angles are exclusively $\approx \frac{\pi}{2}$. The trapezoidal effect is just visible in this distribution with a slightly more pronounced slope after the maximum value, corresponding to the thinner slices of the Newton sphere.

Detection efficiency of ions impinging on a dual MCP chevron stack is known to be dependent on the kinetic energy of ions impinging at the detector[138, 139]. As a result, ions with a lower kinetic energy are less likely to be detected relative to more energetic ions from the same Newton sphere. As the kinetic energy of

impinging ions is strongly affected by the PEISI pulse, there is also a strong ToF dependence. Kinetic energy-dependent detection efficiencies were approximated as the absolute detection efficiencies of Ar^+ ions as calculated by Hosokawa *et al.*[139]. Each PImMS timebin was assigned a detection efficiency based on the average kinetic energy of the constituent ions and the ToF intensity scaled accordingly. This is shown in Panel B of Figure 3.9 where simulated ToF traces with unity detection efficiency (UDE) and a differential detection efficiency (DDE) are shown for three repeller voltages. At high repeller voltages ($V_R = 3 \text{ kV}$), there is no effect on the ToF trace. However, at lower repeller voltages there is a notable decrease in intensity at later ToFs and the effect is especially marked at the lowest repeller voltage.

This is an effect that should be considered given that the PEISI technique differentially accelerates ions. Ions that are not accelerated by the PEISI pulse are therefore detected less efficiently resulting in an observed decrease in intensity at later times-of-flight. The effect is accentuated at lower repeller voltages as these ions gain the least kinetic energy from the extraction field initially. This effect will be explored in greater detail later in the Chapter.

It has been shown that a variety of factors affect the total ion arrival time spread and the overall shape of the ToF profile. In the next section, an overview of the experimental methods will be outlined and then experimental results will be presented.

3.4 Experimental Methods

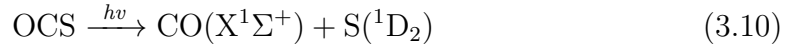
A brief summary of the experimental apparatus will be given in this section. A more detailed discussion of the Oxford Spectrometer may be found in Chapter 2. A gas mixture of 5% OCS, in He (supplied by BOC), with a backing pressure of 1 bar was introduced into an ultrahigh vacuum experimental chamber through a General valve and a 1 mm skimmer. The molecular beam passes through an aperture in the repeller plate before it was crossed with vertically polarised UV pulse ($\approx 10 \text{ ns}$). OCS parent molecules were photodissociated at these wavelengths in a one-photon process. The same UV pulse subsequently photoionised the CO

(CO* ($B^1\Sigma^+$ or $C^1\Sigma^+$)) or S (1D_2) photofragments in a (2+1) resonance-enhanced multi-photon ionisation (REMPI) scheme.

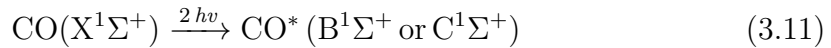
3.5 Experimental Results

In this section, results from the proof-of-principle 3D PEISI imaging experiment are presented for the well-studied one colour UV photodissociation of OCS[143–157]. CO⁺ and S⁺ ions resulting from the photodissociation and subsequent REMPI at around 230 nm were imaged under PEISI conditions with the PImMS2 sensor

OCS molecules were dissociated by a single photon to produce CO($X^1\Sigma^+$) and S(1D_2) photofragments:



CO photofragments are formed in highly excited rotational states. These rotational states, J , of CO photofragments can be probed by absorption of further photons from the same laser pulse to produce CO⁺ ions *via* a (2+1) REMPI scheme[158, 159]:



The sulfur photofragments are also ionised at slightly longer wavelengths[158]



The REMPI spectrum for CO and S(1D_2) photofragments is shown in Figure 3.10. The CO($X^1\Sigma^+;J$) photofragments are formed with a bimodal rotational distribution. This is a result of two well-known dissociation pathways that OCS can follow. Dissociation to the excited states ($^1\Sigma^-$ and $^1\Delta$) in a linear geometry is forbidden due to selection rules ($\Delta\Lambda = \pm 1$), however, excitation is weakly allowed in a bent configuration. The excited states $^1\Sigma^-$ and $^1\Delta$ become $2^1A'$

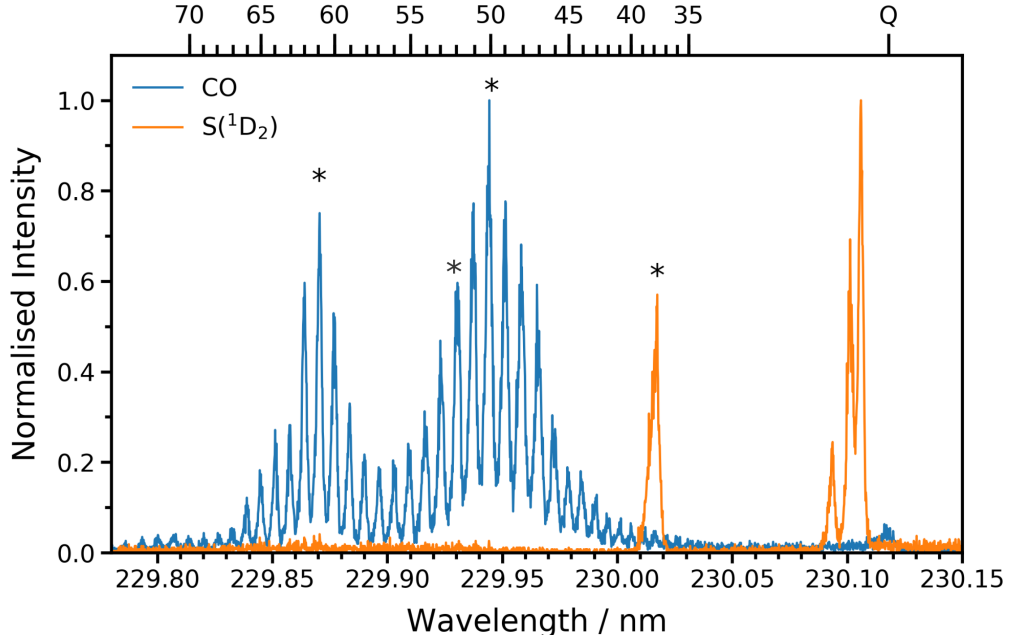


Figure 3.10: The REMPI spectrum for CO (blue) and S (orange) photofragments at around 230 nm is shown. The bimodal structure in the CO is a result of two pathways existing from the excited surface and is detailed in the text. The rotational states of the CO photofragment are labelled on the upper x -axis. Peaks marked with an asterisk relate to CO photofragments that are discussed in this Chapter.

and $2^1 A''$, and $1^1 A''$, respectively. The photodissociation at these wavelengths occurs predominantly *via* the $2^1 A'$ state producing rotationally hot, vibrationally cold $\text{CO}(X^1\Sigma^+)$ photofragments. The bimodal distribution arises from either direct dissociation from the $2^1 A'$ state or surface crossing to the ground state $1^1 A''$. The high rotational states are accessible due to the large torque exerted on the CO photofragments as the parent transitions from a linear structure to a bent configuration[147, 150, 158–163].

3.5.1 Quantitative Measures

To test the quality of imaging under PEISI conditions a number of benchmarks will be used to quantify and compare the technique with other imaging methods.

Slicing Resolution

The first quantitative measure of an imaging technique is its slicing resolution. This measure determines the fraction of a Newton sphere, typically the central

slice, that the imaging technique can record. The smaller the fraction the greater the slicing resolution as this is a closer approximation to the infinitesimally thin slice required to describe the whole three-dimensional velocity distribution of a cylindrically symmetric distribution. The slicing resolution is defined:

$$\frac{\delta t}{\Delta t} = \frac{1}{N} \quad (3.15)$$

where δt is the minimum time gate possible to detect part of the Newton sphere and Δt is the total time of arrival of the Newton sphere. For experiments using PImMS2 this is simplified to the reciprocal of the number of PImMS2 timebins, N , that a specific ion occupies.

Velocity Resolution

The second quantifiable parameter is the velocity resolution, $\delta v/v$, where δv is the width of a feature in a PImMS image at a radius, v . The velocity resolution determines how well features are resolved spatially in an image.

The velocity resolution is typically calculated for the central slice image. It is calculated by fitting the velocity distribution to a Gaussian function:

$$f(v) = A \exp\left(-\frac{(v - \mu)^2}{2\sigma^2}\right) \quad (3.16)$$

where A , v , μ , and σ are the amplitude, velocity, central velocity, and the standard deviation, respectively. The velocity resolution, $\delta v/v$ is inferred from these parameters and is defined:

$$\delta v/v = \frac{\text{FWHM}}{\mu} = \frac{2\sqrt{2\ln 2} \sigma}{\mu} \quad (3.17)$$

where FWHM is the full width at half maximum of the Gaussian.

Angular distribution

The angular distribution is a good measure of the spatial resolution of ion images. The angular distribution of photofragments following a one-photon photodissociation was given in Equation (3.7). The anisotropy parameter, β ranges from +2 for a $\cos^2 \theta$ distribution and -1 for a $\sin^2 \theta$ distribution.

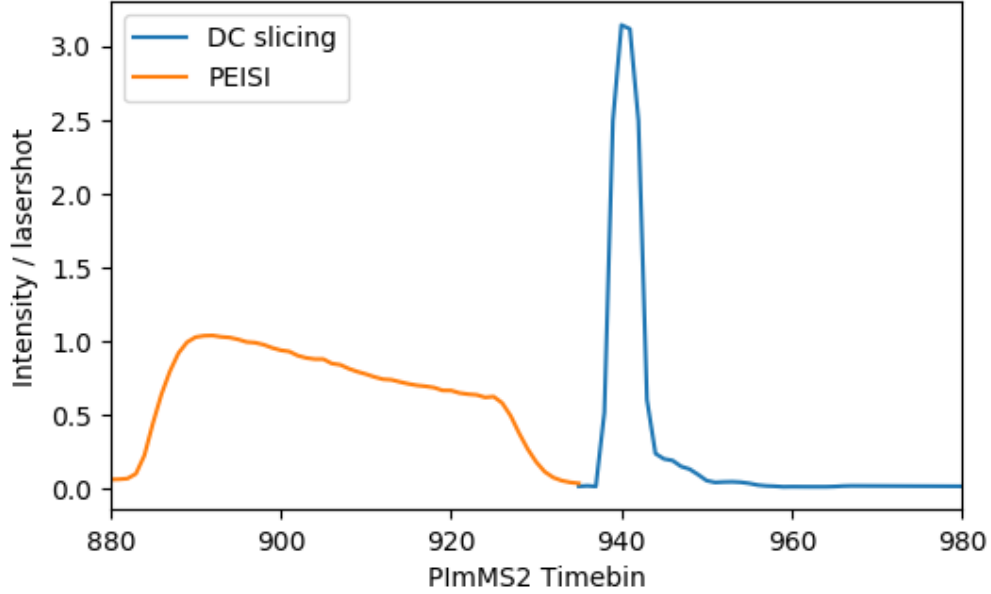


Figure 3.11: Time of Flight spectra recorded under PEISI and DC slicing conditions following the UV photodissociation of OCS at 229.94 nm. The photofragment recorded is CO($J=50$). $V_R = 1$ kV; $V_P = 3$ kV; $t_P = 2.19 \mu\text{s}$.

3.5.2 High Extraction Field

This section will compare experimental data recorded under both DC slicing and PEISI conditions and quantitatively compare the two techniques at a relatively high extraction field ($V_R=1$ kV) and a pulsed extraction field, $V_P=3$ kV. Two different rotational states of CO will be analysed and discussed. A switch time, t_P , of $2.19 \mu\text{s}$ was used, optimised for the CO ion. The velocity and slicing resolutions, and angular distributions will be extracted.

Time-of-flight Analysis

Figure 3.11 shows the time-of-flight spectra following the photodissociation of OCS at around 230 nm under both DC slicing and PEISI conditions. Ions extracted under PEISI conditions have a shorter time-of-flight relative to ions extracted under DC slicing conditions. The ToF spectrum obtained under PEISI conditions has a much larger ion arrival time spread, as expected. Further the trapezoidal profile shape predicted through Simion simulations is observed. The ion arrival time spreads are

51 ($1.3\ \mu\text{s}$) and 7 ($0.18\ \mu\text{s}$) PImMS2 timebins, respectively. These correspond to slicing resolutions of 2.0 % and 14.3 %, respectively. Therefore, in the former case each PImMS2 image captures 2 % of the Newton sphere along the ToF axis. This is a significant improvement in comparison to DC slicing. Previous 3D imaging experiments using PImMS reported by Amini *et al.* in DC slicing reported a slicing resolution of 9 %. This was performed under identical experimental conditions imaging a Newton sphere of CO^+ ions with a comparable velocity distribution. The experiment was performed using a PImMS1 sensor. The PImMS1 sensor has a higher timing resolution than PImMS2, of 12.5 ns but a smaller pixel array resulting in a worse spatial resolution. The enhanced timing resolution explains the improvement in slicing resolution observed by Amini *et al.* in DC slicing conditions. However, despite the reduced timing resolution of PImMS2 used in the PEISI experiments, the slicing resolution is markedly improved. This allows for well-resolved images of the Newton sphere to be recorded over the duration of the arrival time. This will be investigated in the next section.

3D imaging

As mentioned, the use of event-triggered time-stamping cameras such as PImMS, allows images to be recorded throughout the ion arrival time. A series of images recorded by PImMS from the PEISI experiment discussed above are shown in Figure 3.12.

Successive images correspond to the image recorded by PImMS at a specific time-of-flight from the ToF spectrum in Figure 3.11. For conciseness, images shown are from every third PImMS timebin. One can see that the central slice image (timebin 909) qualitatively displays an excellent velocity resolution. Images recorded away from the central slice comprise ions with a larger solid angle of the Newton sphere and are therefore inherently less well-resolved. The PEISI pulse however elongates the Newton sphere sufficiently such that well-resolved images may be recorded in a majority of timebins. This is observed in the 3D images which show consistently single sharp features, except for the caps of the Newton sphere. This is

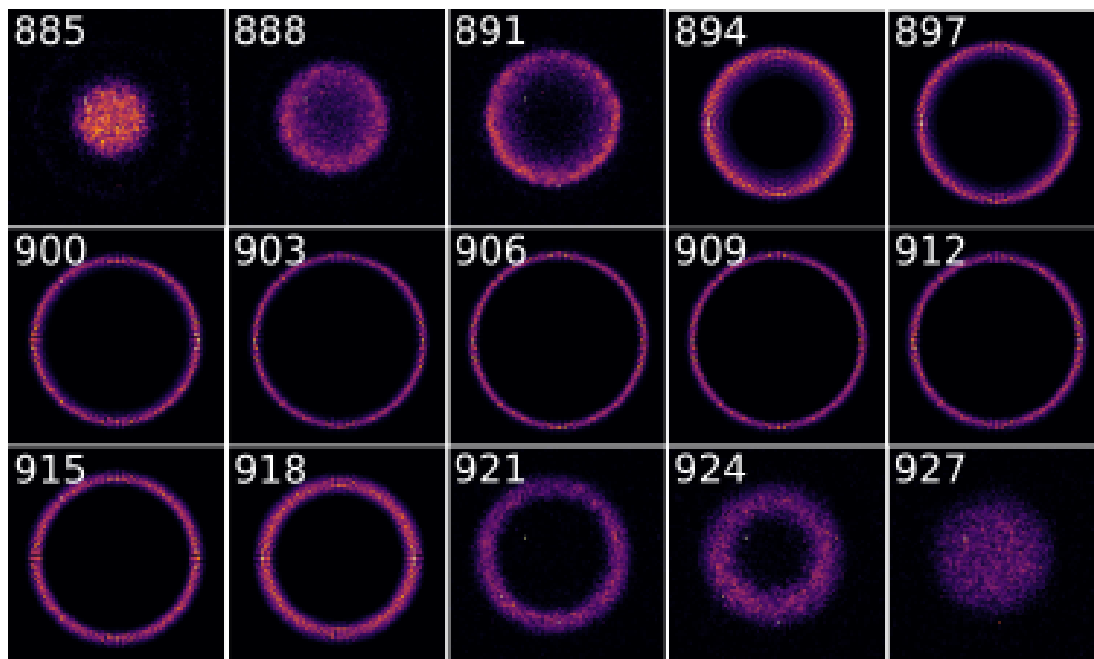


Figure 3.12: Images of the Newton sphere of CO($J = 50$) ions recorded by PImMS2 under PEISI conditions. Images shown were recorded at the labelled PImMS timebin corresponding to the image at the ToF in Figure 3.11.

a powerful demonstration of the ability of PEISI to record the full three-dimensional velocity distribution of photofragments.

Velocity resolution

The velocity resolution of the central slice images was calculated by fitting the velocity distribution of the central slice images to Equation (3.16). The velocity distributions and corresponding Gaussian fits for both imaging techniques are displayed in Figure 3.13.

The velocity resolution is increased from 11.8% under DC-slicing conditions to 6.6% under PEISI conditions. The image arising from PEISI conditions is a clear sharp peak with little or no contributions from parts of the Newton sphere out of the central slice plane. This is not true for the velocity distribution extracted under DC slicing conditions, where a tail toward lower radii is clearly visible and is due to out of plane contributions. Under both conditions, the velocity distribution tails off after the peak. This is due to the existence of CO photofragments arising from different parent molecules. The first of these photofragments derive from

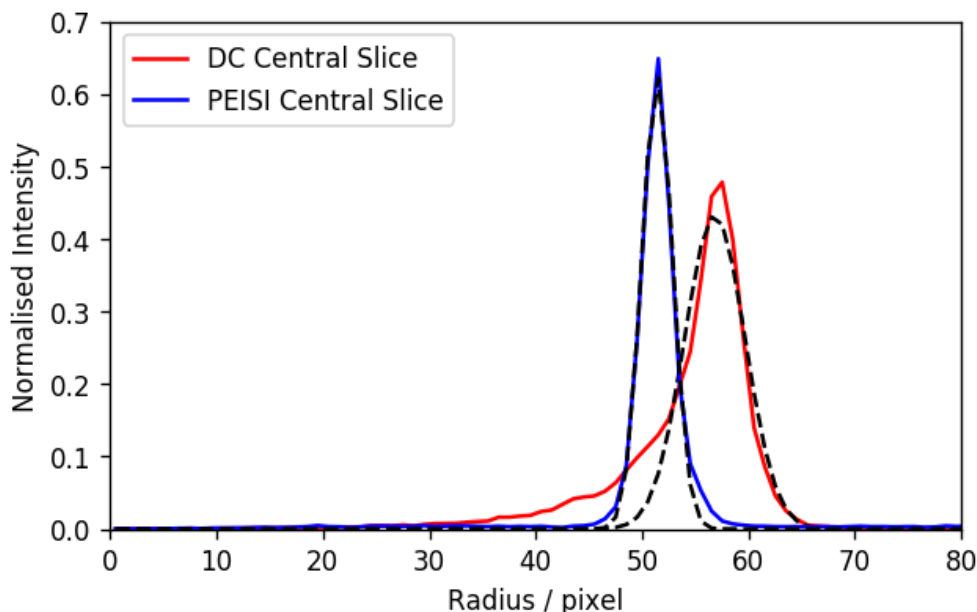


Figure 3.13: Comparison of the velocity distribution of $\text{CO}(J = 50)$ photofragments extracted from the central slices obtained under PEISI and DC slicing conditions. Each distribution is fitted to Equation 3.17 to obtain the velocity resolution (black dashed lines). See text for more details.

parent molecules in an excited vibrational state also present in the molecular beam. As the molecular beam was not focussed with a hexapole there is an ensemble of rotational and vibrational states present in the molecular beam. The second of these photofragments arise from the photodissociation of isotopic OCS ($m = 62 \text{ g mol}^{-1}$) molecules. The heavier sulfur isotope results in a CO photofragment with a larger velocity. The two photofragments lie very close in velocity (ratios of 1.063 and 1.014 relative to the peak velocity) and are not resolved at these extraction voltages. Therefore these CO photofragments are manifest in the velocity distributions at velocities slightly greater than the peak velocity. As the parent molecules, $\text{OC}^{34}\text{S}(v_2 = 0)$ and $\text{OC}^{32}\text{S}(v_2 = 1)$, that give rise to these CO photofragments are much less abundant than the $\text{OC}^{32}\text{S}(v_2 = 0)$, the contribution to the velocity distribution is less significant. However, under these experimental conditions the respective velocity features cannot be resolved.

The velocity peak is shifted to lower radii under PEISI conditions relative to DC slicing conditions. Under PEISI conditions, the overall times-of-flight are reduced

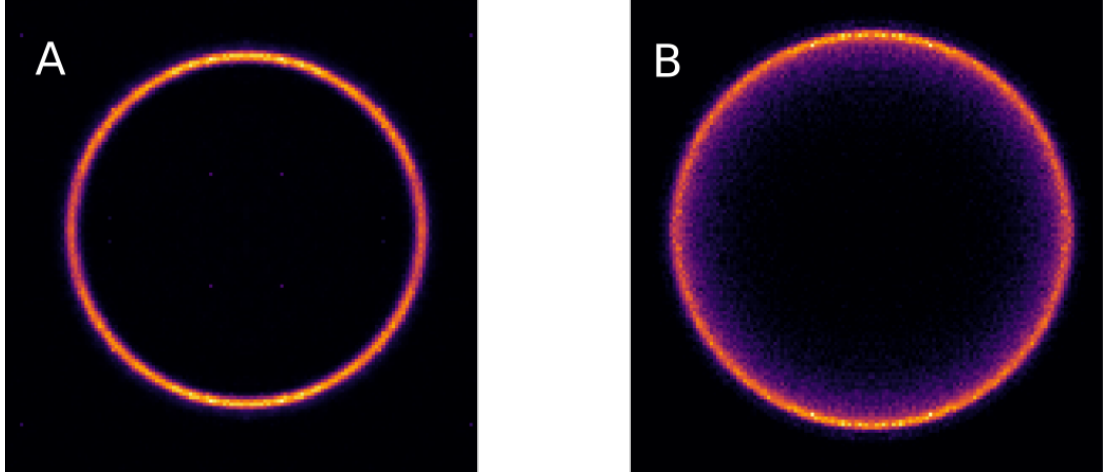


Figure 3.14: Central slice images of the $\text{CO}(J = 50)$ photofragment recorded under PEISI (Panel A) and DC slicing (Panel B) conditions.

(see Figure 3.11) while the initial velocity of photofragments is unchanged thus the extent of the ion Newton sphere at the detector is reduced and a smaller image is recorded.

Angular Distribution of CO Photofragments

The angular distribution of the $\text{CO}(J = 50)$ and $\text{CO}(J = 62)$ photofragments will be discussed (marked on the REMPI spectrum in Figure 3.10). The lower rotational state photofragment arises from two pathways which results in a near isotropic velocity distribution as the perpendicular and parallel transitions partially cancel each other out. However, the higher rotational states are formed predominantly from a parallel transition and hence display a highly anisotropic image[158–160].

Figure 3.14 shows the central slice images of the $\text{CO}(J = 50)$ photofragment recorded by PImMS under PEISI (Panel A) and DC slicing (Panel B) conditions. The spatial anisotropy parameter of the $\text{CO}(X^1\Sigma^+; v = 0|J = 50)$ photofragment angular distribution has been extracted from the central slice recorded by PImMS under PEISI conditions and compared to that extracted under DC slicing conditions. A β parameter of 0.18 ± 0.01 was measured under PEISI conditions. This is in comparison to 0.17 ± 0.01 extracted under DC slicing conditions using the central recorded slice. They are in reasonable agreement and are in good agreement with work performed by Van den Brom *et al.*[150] who reported a anisotropy parameter

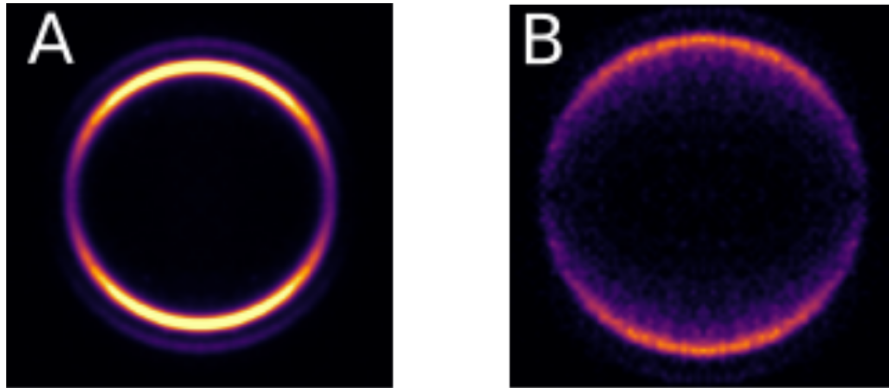


Figure 3.15: The central slice images of the $\text{CO}(J = 62)$ photofragment recorded under PEISI (Panel A) and DC slicing (Panel B) conditions.

of 0.17 ± 0.01 . This work employed a hexapole to state select $\text{OCS}(v_2 = 0 | JM = 10)$ molecules (where M refers to the splitting of the degenerate rotational states in the presence of an electric field). In the present work, an ensemble of quantum states of OCS are present, notably in the $v_2 = 1$ OCS bending mode.

The β parameter of the $\text{CO}(X^1\Sigma^+; v = 0 | J = 62)$ photofragment angular distribution has been extracted in the same manner. A β parameter of 1.40 ± 0.01 was extracted from the central slice under PEISI conditions. An analogous result of 1.45 ± 0.02 was extracted from the Abel inverted image under DC slicing conditions. The central slice recorded by PImMS under PEISI and DC slicing conditions are shown respectively in Panels A and B of Figure 3.15. Both display a highly anisotropic distribution as is expected for this photofragment[160]. These values are in reasonable agreement though show a slight difference. The minor feature at higher velocities observed in Panel A corresponds to the photodissociation of vibrationally excited OCS molecules.

3.5.3 Low extraction field

This section will compare experimental $\text{CO}(J = 52)$ photofragments imaged under both DC slicing and PEISI conditions and quantitatively compare the two techniques. Experiments discussed in this section are identical to that of Section 3.5.2.

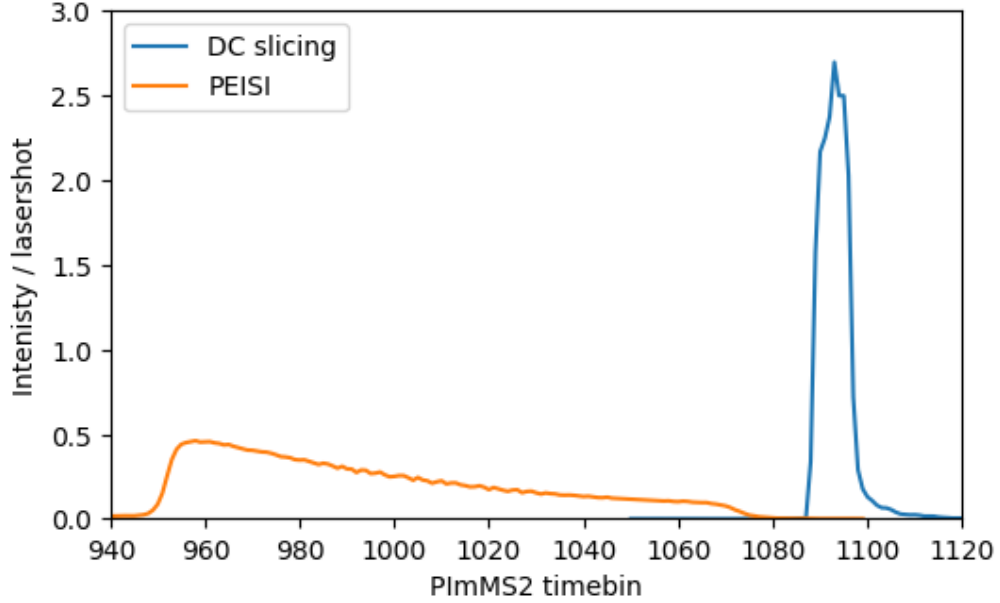


Figure 3.16: A comparison of the ToF spectra recorded under DC slicing and PEISI conditions with a repeller voltage of 500 V. The ToF spectra were recorded at wavelengths producing the $\text{CO}(J = 52)$ photofragment.

Time-of-flight Analysis

Figure 3.16 shows the time-of-flight spectra of the $\text{CO}(J = 52)$ photofragment resulting from DC slicing and PEISI conditions with a repeller voltage, V_R , of 500 V and pulsed voltage, V_P of 3 kV. The ion arrival time spread is notably increased under PEISI conditions, as expected. Both spectra are normalised to the total number of acquisitions. The average intensity per timebin is much less under PEISI conditions in comparison to DC slicing. This is because, assuming that the molecular beam flux and laser intensity are comparable, then the total amount of CO photofragments produced in each experiment are the same. However, under PEISI conditions, the Newton sphere arrives at the detector over a much longer time spread and hence fewer ions are recorded per timebin.

Under PEISI conditions, the Newton sphere spans 128 PImMS2 timebins, corresponding to a slicing resolution, $\delta t / \Delta t = 0.78\%$. This is in comparison to an ion arrival time of 20 timebins and a slicing resolution, $\delta t / \Delta t = 4.76\%$ under DC- slicing. This is in comparison with previous 3D imaging work with PImMS

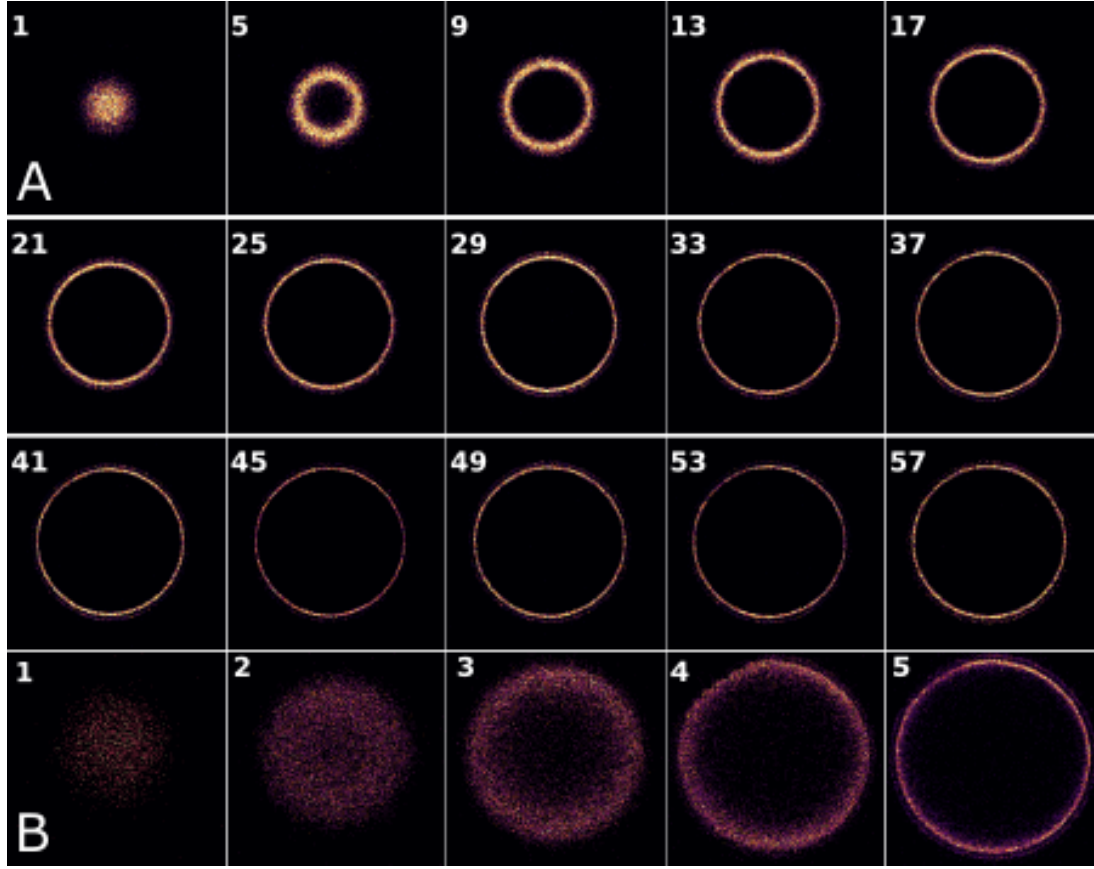


Figure 3.17: Panel A shows a selection of $\text{CO}(J = 52)$ photofragment PImMS2 images recorded through the Newton sphere under PEISI conditions. Panel B shows the corresponding images recorded under DC slicing conditions. The number corresponds to the relative timebin through the Newton sphere. Images are only shown for the first half of the Newton sphere.

performed by Amini *et al.*, who achieved a 9% slicing resolution and 2% slicing resolution reported in Section 3.5.2. These numbers are not directly comparable, as those experiments were performed under higher extraction fields ($V_R = 1 \text{ kV}$) and therefore fewer slices are to be expected.

3D imaging

The use of PImMS allows images of the entire Newton sphere to be recorded in both DC slicing and PEISI. The slice images through the Newton sphere will be discussed in this section. Figure 3.17 shows slice images through the Newton sphere under PEISI conditions (Panel A) and in DC slicing (Panel B) up until the central slice along the ToF axis and respective PImMS timebin is labelled

in the top left of each image. The images are nearly symmetric around this point the central slice and have therefore been omitted. In Panel A, every fourth PImMS image is shown for conciseness. This Figure shows the extraordinary 3D capabilities of PEISI in combination with an event-triggered timestamping camera like PImMS. More than one hundred PImMS images are recorded for a single photofragment under PEISI conditions.

The respective central slice images recorded by PImMS under PEISI and DC slicing conditions are shown in Panels A.57 and B.5. The PEISI recorded central slice appears to better resolved than the analogous image recorded under DC slicing conditions. A comparison of the velocity distributions of the central slice images and respective resolutions are shown in Figure 3.18.

Two peaks are resolved in each experiment. The major peak corresponds to CO photofragments derived from OCS molecules (and from the isotopic OC^{34}S) in the ground state and the minor peak is the sum of contributions from OCS molecules with a quantum of excitation in the bending vibrational mode. The minor peak is more clearly resolved under PEISI conditions in the central slice images. This peak was not resolved in the data shown in Section 3.5.2 and overlapped with the major peak. The DC slicing central slice image has a tail toward lower velocities as the central slice recorded by PImMS includes ion contributions from a larger part of the Newton sphere and hence a larger solid angle. The velocity resolutions of both rings and imaging techniques are summarised in Table 3.2. The Abel inverted image has introduced noise throughout the image and radii greater and smaller than where the rings are in the image.

A high velocity resolution is retained not only toward the central time slice, as in DC slicing and Panel B, but also toward the extreme times-of-flight. The central slices derived from each method (Panel A: 57; Panel B: 5) are comparable, though the velocity resolution is slightly better under PEISI conditions, see Table 3.2. Moving away from the central slice in DC slicing, the images quickly become poorly resolved as ions from a range of inclinations are averaged across the timebin resulting in the blurred images observed. However, under PEISI conditions, the

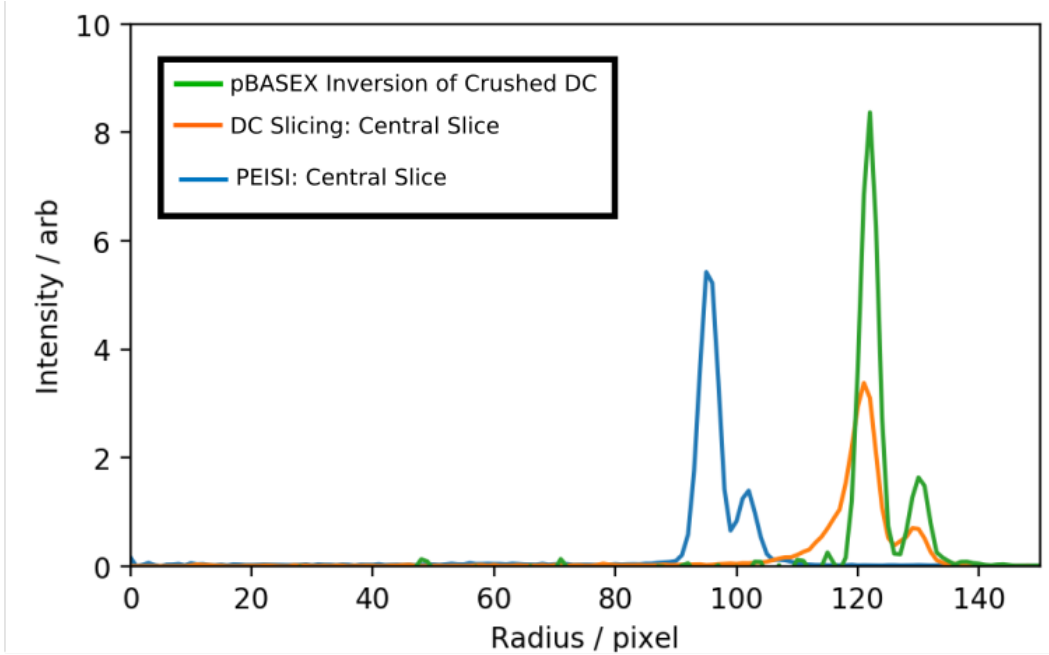


Figure 3.18: The respective velocity distributions of the central slice and Abel inverted images of the $\text{CO}(J = 52)$ photofragment recorded under PEISI and DC slicing conditions are shown.

velocity resolution is not as greatly affected as the DC slicing analogues until $\approx$ PImMS timebin 21 where there is a slight drop in sharpness. The velocity resolution does not deteriorate to DC slicing levels until around the fifth PImMS timebin.

This is illustrated in Figure 3.19 which plots the normalised velocity distribution of each PImMS timebin through the ToF profile. The width of the arc represents the FWHM of the image rings and hence how sharp the velocity resolution is. The width is thinnest at the central slice which is expected as there is the smallest contribution of velocity along the ToF direction perpendicular to the molecular beam and

Method	$\Delta v/v$
PEISI: $v = 0/\text{OC}^{34}\text{S}$	0.039
DC: $v = 0/\text{OC}^{34}\text{S}$	0.051
Abel: $v = 0/\text{OC}^{34}\text{S}$	0.028
PEISI: $v = 1$	0.038
DC: $v = 1$	0.038
Abel: $v = 1$	0.028

Table 3.2: Measured velocity resolutions of the $\text{CO}(J = 52)$ photofragments under DC slicing and PEISI conditions

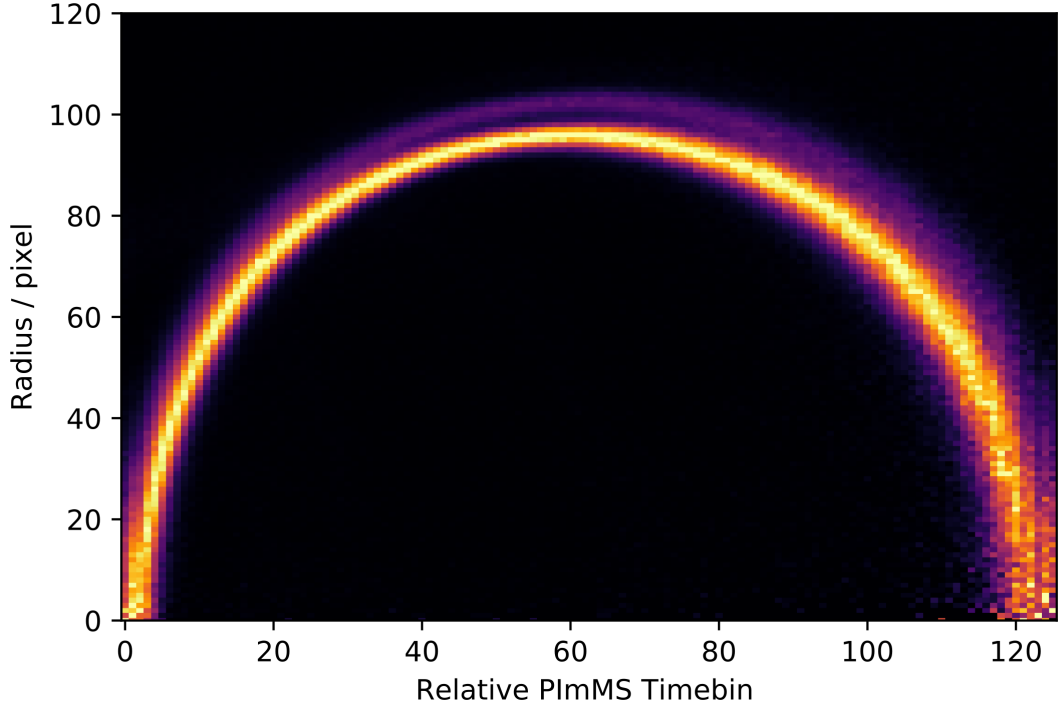


Figure 3.19: The velocity distribution as a function of PImMS timebin is shown for this CO photofragment. See text for more details.

therefore a higher attainable velocity resolution. The velocity resolution degrades away from the central slice due to the increased contribution of the molecular beam velocity. At the ToF extrema, the velocity resolution is reduced to $\approx 10\%$ [164].

The second half of the image is slightly worse resolved. This is a consequence of the ToF velocity component not mapping linearly with ToF. The later arriving half of the Newton sphere is stretched less than the first half and the velocity resolution decreases as a result. In the very earliest and latest timebins there is an unavoidable loss of velocity resolution on account of ions arriving at the caps of the Newton sphere and are ions are crushed over a large number of velocities.

Angular Distribution of CO Photofragments

The β parameter of the $\text{CO}(J = 52)$ photofragment angular distribution has been extracted from the central slice recorded by PImMS under PEISI conditions and compared to that extracted under DC slicing conditions and the reconstructed central slice following the Abel transform. A β parameter of 0.30 ± 0.01 was measured

under PEISI conditions. This is in comparison to 0.30 ± 0.01 and 0.31 ± 0.01 extracted under DC slicing conditions using the central recorded slice and the Abel inverted image, which excellent agreement. They are also in good agreement with the work done by van den Brom *et al.*[150] who reported a value of 0.25 ± 0.03 . Again, exact agreement is not expected as van den Brom *et al.* employed a hexapole to state-select $\text{OCS}(v_2 = 0|JM = 10)$ molecules, whereas in the current work an ensemble of rovibrational states are present.

3.5.4 Detection Efficiency of Ionic Photofragments

With the spatial anisotropy parameter of the angular distribution of photofragments ascertained it is possible to attempt to calculate the relative kinetic energy dependent detection efficiencies for CO^+ ions. The β parameter dictates the shape of the time-of-flight profile as discussed in Section 3.3.2. Also discussed in this Section was the effect that ion kinetic energy at the detector has on the efficiency that an ion is detected. As a result, differential kinetic energies between ions at the front and back of the Newton sphere cause a difference in detection efficiency of these ions. This ultimately has the effect of an apparently lower intensity for ions at longer times-of-flight in comparison with simulated data that has assumed a 100 % detection efficiency of ions.

The experimental ToF profile recorded with a repeller voltage of 0.5 kV and a pulsed voltage of 3 kV is shown in Figure 3.20. The peak corresponds to CO^+ ions deriving from the $J=52$ rotational state. Also shown are two simulated ToF spectra of CO^+ ions with the velocity distribution of the $J=52$ following UV photodissociation. The orange trace assumes an isotropic distribution of ions while the green trace assumes an angular distribution governed by the experimentally determined β value of 0.30. The number of PImMS timebins that comprise the Newton sphere is the same for both the simulated and experimental data. This shows that the experiment is well understood. Each profile has been area normalised.

The difference between the simulated isotropic and anisotropic ToF profiles is small but distinct. There is a slight preference for ions to arrive toward the central

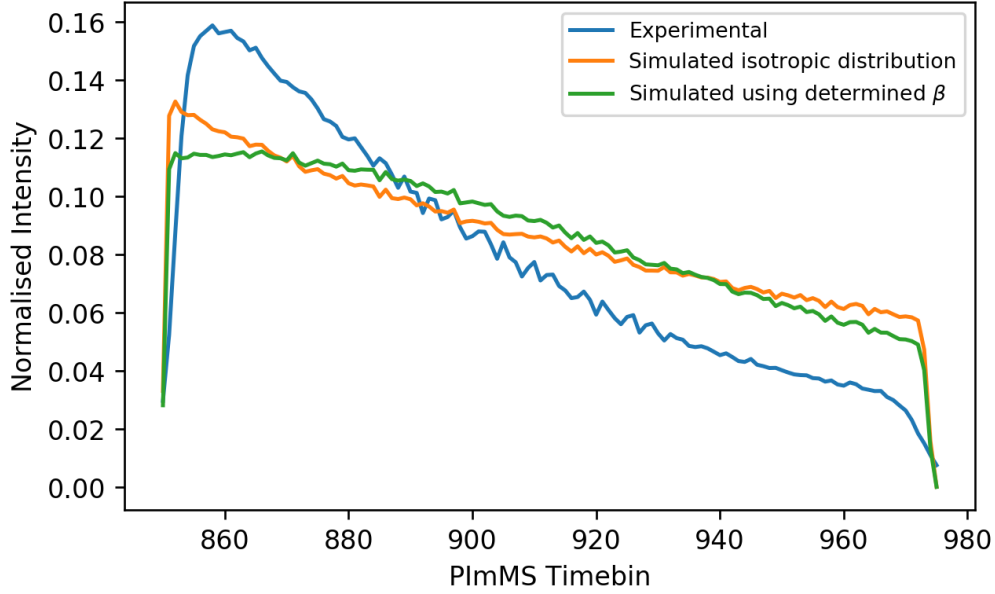


Figure 3.20: Simulated and experimental ToF profiles for $\text{CO}(J = 52)^+$ ions are shown. The experimental ToF profile is shown in blue, the isotropic simulated distribution is shown in orange, and the simulated ToF profile accounting for the spatial anisotropy parameter is shown in green.

slices of the Newton sphere relative to the termini. This is expected for distributions with a positive spatial anisotropy parameter and was discussed in Section 3.3.2.

However, the experimental data markedly differs from the simulated spectra. The experimental data do show a trapezoidal shape but it is greatly exaggerated at short and long times-of-flight. The earliest arriving ions have a greater than simulated intensity and the opposite for the latest arriving ions. The observed decrease in intensity for the late arriving and hence least energetic ions is qualitatively consistent with a differential detection probability.

Panel A of Figure 3.21 shows the simulated kinetic energies of ions at the detector. The peak in kinetic energy at around 1.4 keV is due to the anisotropic angular distribution. This is the final kinetic energy of the ions that are most likely to be formed in this distribution. Panel B shows the probability distribution of ions detected experimentally as a function of impacting kinetic energy. Each kinetic energy value was determined through the average of simulated kinetic energies of

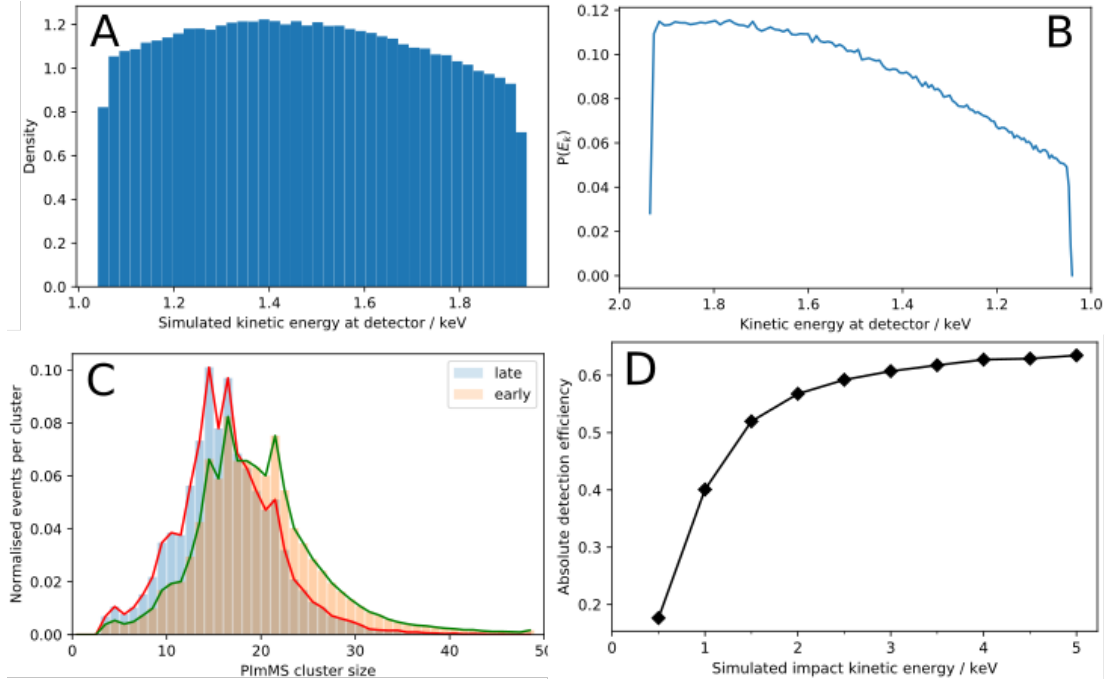


Figure 3.21: Panel A shows the simulated kinetic energy distribution of ions at the detector at these voltages. Panel B shows the experimentally determined effective kinetic energy probability distribution as may be recorded by a PImMS2 camera. Panel C shows the histogram of cluster sizes as recorded by PImMS2 depending on whether the ion arrived early or late in the ToF profile. Panel D shows the absolute detection efficiency of argon ions as reported by Hosokawa *et al.*[139] which may be loosely used for a model of the CO ions.

ions within each PImMS timebin. The kinetic energy scale has been inverted to reflect the inverse relationship between kinetic energy and time-of-flight.

Panel C shows the histogram of cluster size of ions after centroiding arriving in the first and last ten PImMS timebins of the ToF profile. Larger clusters correspond to brighter flashes detected by PImMS. Brighter flashes emitted by the detector derive from ions impacting on the front face of the detector harder *i.e.* with more kinetic energy. The histogram shows that ions arriving in the first ten timebins are shifted to higher cluster sizes than those arriving late. The average PImMS cluster size of ions arriving early is 19 compared to 15 for that of the late arriving ions. This shows that on average these ions are detected as brighter flashes and hence are therefore more likely to be detected in general. This implies that there is a differential detection efficiency between the early and late arriving ions. Panel D shows the absolute detection efficiencies of Ar^+ ions measured using the coincidence

method for neutralised incident ions and ionised target ions in electron capture collisions performed by Hosokawa *et al.*[139]. The detection efficiency increases with impact kinetic energy plateauing at around 63% efficiency, the open area ratio, OAR, of the detector used — a good measure of the maximum detection efficiency of an MCP detector.

Hosokawa *et al.* were able to evaluate absolute detection efficiencies by employing coincidence detection to detect both the charged and neutral species at separate detectors. The number of ions detected at the separate detector, n is given by:

$$n = n_B + \kappa \epsilon_r \sigma \pi I \quad (3.18)$$

where n_B is the number of background ions, κ is the transmission of the ToF tube, ϵ_r is the detection efficiency of the separate MCP detector, σ is the one electron-capture cross-section, π is the thickness of the ion beam, and I is the count-rate of the incident ion beam.

The number of ions detected at the other detector in coincidence, C is given by

$$C = \kappa \epsilon_r \epsilon_0 \sigma \pi I \quad (3.19)$$

where ϵ_0 is the absolute detection efficiency of the detector that is interested in. By combining Equations (3.18) and (3.19) the absolute detection efficiency of the detector in question is given by:

$$\epsilon_0 = \frac{C}{n - n_B} \quad (3.20)$$

In a later paper from the same group, Takahashi *et al.*[138] describe the detection efficiency curves quantitatively by relating the absolute detection efficiency, ADE, to the secondary electron emission, γ' , from the surface of the MCP caused by an incident ion and arrive at the following relation:

$$\text{ADE} = \text{OAR} - 0.75 \exp(-0.035\gamma') \quad (3.21)$$

where OAR is the open area ratio and equivalent to the maximum absolute detection efficiency. For ions of the same mass impinging on the same detector, the secondary

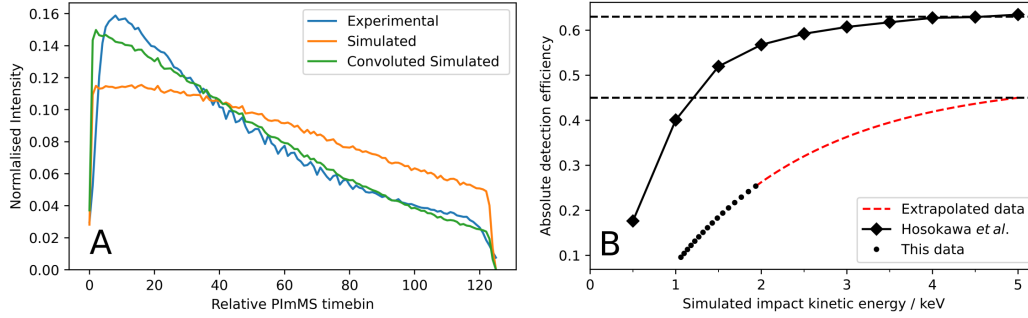


Figure 3.22: Panel A shows the experimentally determined ToF profile (blue); the simulated ToF profile for the experimentally determined angular distribution of ions (orange) with a repeller voltage of 0.5 kV; the detection efficient convoluted ToF profile (green). Panel B shows the absolute detection efficiencies of Ar^+ ions determined by Hosokawa[139] and the relative detection efficiencies gleaned from this data, extrapolating to the OAR of the Oxford detector.

electron emission is simply a function of the initial kinetic energy. Therefore the simulated time-of-flight profile, $P(t)$, that assumes a 100% detection efficiency can be modified to include a kinetic energy dependent term, $\eta(E_k)$, that accounts for the differential detection efficiency.

$$P(E_k) = \eta(E_k)P_{\text{sim}}(t) \quad (3.22)$$

The kinetic energy dependent terms, $\eta(E_k)$, are determined by fitting the simulated ToF profile, $P_{\text{sim}}(t)$ to the experimental data through Equation (3.22) where $\eta(E_k)$ obey the relation in Equation 3.21[138]. Figure 3.22 summarises the results of the fitting process. Panel A shows the experimental ToF profile, the simulated ToF profile with the experimentally determined angular distribution, and the simulated ToF profile with the detection efficiency convolution. Each profile has been normalised such that the bound area is equal to unity. The experimental (blue) and simulated (orange) ToF profiles were shown and discussed in Figure 3.20. The convoluted ToF profile (green) is in much better agreement with the experimentally observed ToF profile. The relatively enhanced intensity at early times-of-flight is consistent with that observed experimentally. Further, the intensity at late times-of-flight is also in excellent agreement, matching almost perfectly at the later times. The shape of both are also in excellent agreement *i.e.* where the simulated

ToF profile predicts a strongly trapezoidal shape the experimental data displays a much sharper curved increase. This is predicted very well with the detection efficiency convolution. The only slight discrepancy is the shape of the profile at the very earliest times-of-flight where the observed peak is not quite replicated.

Panel B shows the experimentally determined kinetic energy dependent detection efficiencies for the Oxford detector using this method. It should be noted that these detection efficiencies are only valid for the detector voltages that were used experimentally. Also strictly they may only give insight into the detection efficiency for CO^+ ions as other species are likely to possess different electronic and nuclear stopping powers that ultimately have an effect on the secondary electron emission and hence the respective absolute detection efficiencies. Further, these are not absolute detection efficiencies but rather relative detection efficiencies specific to this experiment. Each data point represents the scaling factor that the corresponding $P_{\text{sim}}(t)$, related to the simulated impacting kinetic energy, in Panel A is multiplied by *i.e.* the transformation from orange curve to green curve. The red dashed line is an extrapolated line converging on the open area ratio for the Oxford detector, 45%. Also shown for reference are the absolute detection efficiencies for Ar^+ ions as determined by Hosokawa *et al.*[139]. Here, the values shown are the *absolute* detection efficiencies on account of the experiment using ion counts in coincidence with a separate detector.

The curve extracted by Hosokawa *et al.* converges at an ADE of 0.63. This is the open area ratio of the detector used in the experiment. Both curves show the trend of an exponential increase in detection efficiency with increasing kinetic energy as is expected. The curve attained by Hosokawa and coworkers exhibits a much steeper rise than was observed in the present data. There are a number of reasons that contribute to this effect. Firstly, the two detectors that are being compared have fundamentally different specifications including size, design, and quality. This inherently means that the ADEs are not necessarily comparable. Secondly, the potential across the MCP detectors was different in the two experiments. In the present work, a potential of 1.9 kV across the front and back of the MCP

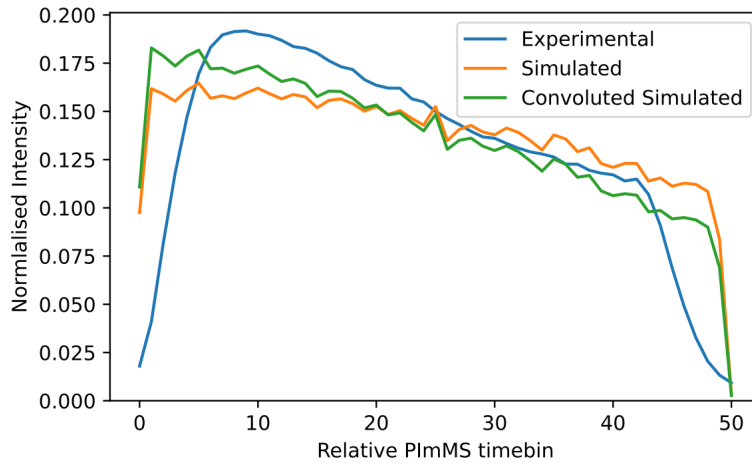


Figure 3.23: The convoluted simulated ToF profile recorded at a repeller voltage of 1 kV in comparison with the experimentally observed ToF profile and the simulated ToF profile, assuming unity detection efficiency.

chevron stack was employed, in comparison to 2.16 kV in the work performed by Hosokawa. Detection efficiency of MCP detectors is well known to increase non-linearly with potential difference[165]. As such even an apparently modest increase of 260 V will result in a much greater ADE as has been observed in the Hosokawa *et al.* work. Another difference between the two experiments is the detection efficiency of the detection scheme that comes after the MCPs. Hosokawa *et al.* employed a wedge-and-strip anode with a detection efficiency of $>80\%$ while the present work employed the PImMS2 camera whose detection efficiency will be different. Finally, the detection of different species in these cases, Ar^+ and CO^+ , would be expected to produce different results on account of differing electronic and nuclear stopping powers..

Figure 3.23 shows the experimental, simulated, and convoluted simulated ToF profile of the PEISI experiment using a repeller voltage of 1 kV. The convolution was performed using the average simulated kinetic energies of the CO^+ ions in each PImMS timebin and the kinetic energy dependent ADEs from Panel B of Figure 3.22. The convoluted simulation is in better agreement than the raw simulated data. The improvements are less clear here as, in general, the final kinetic energies are more narrowly spread and therefore there is a more uniform detection efficiency

across the Newton sphere. However, the convoluted ToF profile does show a relative enhancement and diminution in the earliest and latest arriving ions, respectively, as is observed experimentally.

This section has highlighted an unexpected consequence of PEISI. Although it has been shown that the differential detection efficiency can be accounted for through post-processing, it is important to understand the limitations of the technique. For many applications, uniform detection efficiency of ions throughout the Newton sphere is a necessary condition to ensure democratic treatment of the distribution. Therefore, operating in a regime of saturated detection efficiency would be essential. This could be achieved by increasing the potential difference across the detector or increasing the pulsed voltage, V_p to retain (or increase) the slicing resolution. However, a consideration on the extraction voltage must be made to ensure that ions are not adversely detected.

3.5.5 Multiple Ion Extraction

For a given mass-to-charge ratio, m/z , there is an optimum switch time, t_p , that maximises the elongation of the inverted Newton sphere. This time can be approximated using Simion 8.0 and optimised experimentally. The REMPI of CO and S photofragments at around 230 nm predominantly produces either only CO or S ions. However, at around 230.01 nm, an appreciable amount of both CO^+ (occupying rotational states $J = 40, 41$) and S^+ ions are produced, see Figure 3.10.

By modifying the delay time, t_p , the elongation of either the Newton spheres of CO^+ or S^+ photoions can be optimised. These scenarios are shown in Figure 3.24. Panel A shows the ToF spectrum obtained under DC slicing conditions *i.e.* a pulsed voltage of 0 V. Panels B and C show the ToF spectra obtained with a pulsed voltage of 3 kV applied at switch times of $3.10 \mu\text{s}$ and $2.92 \mu\text{s}$, respectively, corresponding to switch times optimised for S^+ and CO^+ ions, respectively.

The ToF spectrum in Panel A shows CO^+ ions arrive before S^+ ions. The central slice image for each ToF peak is shown adjacent to the corresponding ToF peak (red panel: CO^+ , blue panel: S^+). In Panel B, the ToF peak position corresponding

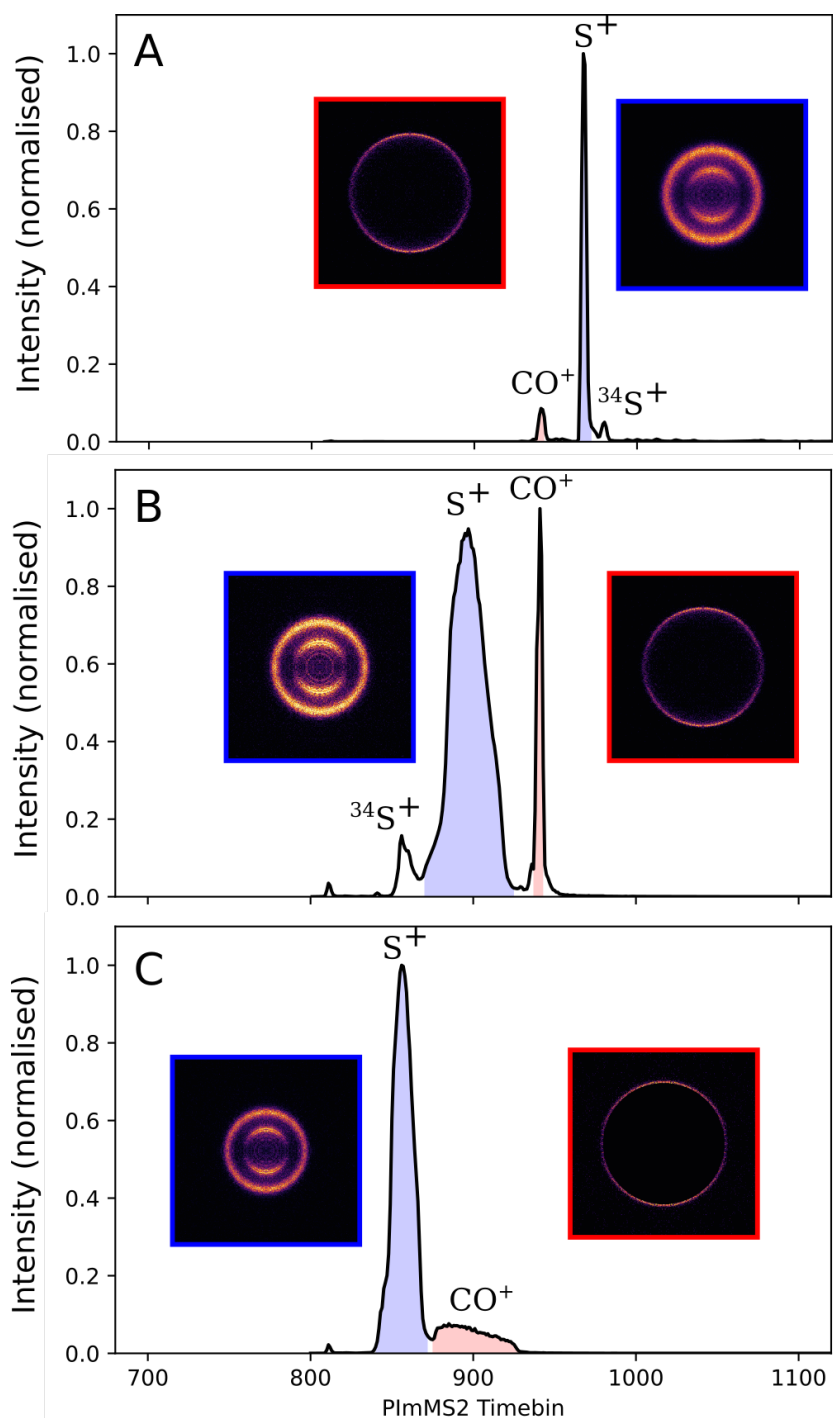


Figure 3.24: The ToF spectra show the CO^+ and S^+ peaks which are simultaneously borne at these wavelengths. Panel A shows the ToF spectrum recorded under DC slicing conditions. Panel B shows the spectrum recorded when t_P is optimised for elongation of the ^{32}S Newton sphere, and the CO Newton sphere remains unchanged. Panel C shows the ToF spectrum obtained where t_P has been optimised for the CO^+ photofragment. In this case the sulfur Newton sphere is also inverted. In each panel the central slice of the CO^+ image is bordered in red and the S^+ in blue.

Method	CO ⁺	S ⁺
DC slicing	12.5%	10%
PEISI (S ⁺ optimised)	12.5%	1.9%
PEISI (CO ⁺ optimised)	2%	3.3%

Table 3.3: Slicing resolutions of each photofragment resulting from each experiment.

to CO⁺ ions is unchanged from Panel A despite the PEISI pulse. This is because at the switch time, the Newton sphere of CO ions has already entered the field-free region and is therefore unaffected by the pulsed electric field. The S⁺ ions are accelerated however, causing a Newton sphere inversion that subsequently arrives at the detector before the CO⁺ photoions. The final Panel shows the effect when the switch time is optimised for the CO⁺ ions. At this time, both Newton spheres are located in the pulsed region. As a result, the Newton spheres of both CO and S photofragments are inverted. As the sulfur Newton sphere experiences the pulsed field for longer, these ions enter the field-free region with a much greater velocity in the ToF direction and arrive at the detector before the CO Newton sphere.

In Panels A and B a third peak is observed. This peak corresponds to ions of the minor isotope of sulfur. The relative peak intensity of the ³⁴S⁺ to the ³²S⁺ is in agreement with the isotopic ratio (4.2%). The peak is also observed in Panel C and has partially merged with the ³²S⁺ peak.

*

Slicing Resolution

The slicing resolution of each Newton sphere and each experiment is outlined in Table 3.3. The slicing resolution of the CO⁺ and S⁺ Newton spheres under optimised PEISI conditions are 2% and 1.9%, respectively. This is a large improvement and in good comparison with PEISI experiments at these extraction voltages discussed earlier in this Chapter. The slicing resolution of CO⁺ ions under optimised PEISI conditions for the sulfur Newton sphere is unchanged from the DC slicing as it is unaffected by the pulsed extraction field as explained previously.

*

Velocity Resolution

The velocity resolution of the CO^+ central slices images under PEISI and DC slicing conditions are 5.2% and 13.6%, respectively. The velocity distributions for each are shown in Panel A of Figure 3.25. The velocity resolutions are slightly enhanced compared with those of the carbonyl fragments presented earlier in this Chapter under the same extraction conditions. This is because the Newton sphere of CO photofragments is travelling faster as a result of the lower rotational states occupied. The images were accumulated over the wavelength range corresponding to the resonantly enhanced ionisation S^+ peak. This wavelength range corresponds to resonant enhanced ionisation of multiple rotational states of the CO photofragments. Hence the CO^+ image is an average of the velocity distribution of multiple rotational states. The two CO photofragments can be assigned individually for each shot of the REMPI scan and therefore be analysed separately. The velocity resolution is enhanced to 3.5% for both fragments as a result. The velocity distributions of the resolved CO photofragments are shown in Panel B of Figure 3.25 and have different peak velocities.

The velocity resolution of the S^+ central slices is harder to quantify due to the well-known bimodal ‘slow’ and ‘fast’ features that are present. For each rotational state of CO, there is a correlated sulfur photofragment with a unique velocity distribution. This manifests as an individual ring in the sulfur image with a unique angular distribution. Therefore there are as many sulfur rings in the image as rotational states of CO populated. Further, there are unique sulfur features correlated to the different vibrational states of the parent molecules. Therefore for this experiment where hexapole focussing was not employed to state select the parent molecules, there is the possibility of over fifty features, of varying intensity, present. However, the velocity resolution can be approximately quantified by measuring for the ‘slow’ and ‘fast’ Newton spheres separately. These originate from the bimodal feature of the CO REMPI spectrum. As the carbonyl and sulfur photofragments are correlated it makes sense that a bimodal distribution is reflected in the velocity

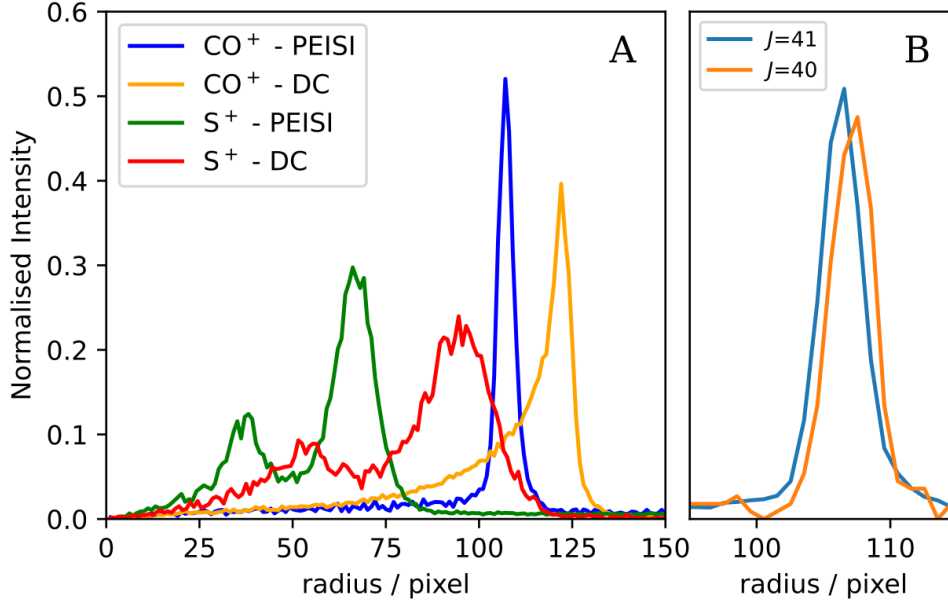


Figure 3.25: Panel A shows the velocity distribution of the S(¹D₂) and CO($J = 40, 41$) photofragments recorded under PEISI conditions, where both ion Newton spheres are elongated ($t_p = 2.92 \mu s$ and $V_p = 3 kV$) and under DC slicing conditions. Panel B shows the resolved CO ($J = 40, J = 41$) rotational states' velocity distributions.

Photofragment (Technique)	$\Delta v/v$
CO (DC)	13.6%
CO (PEISI)	5.2%
CO ($J=40$) (PEISI)	3.5%
CO ($J=41$) (PEISI)	3.5%

Table 3.4: Velocity resolutions of each image and corresponding imaging method.

distribution of sulfur ions. As all sulfur photoions are ionised at the same wavelength, they all appear in the same image as features at different velocities.

*

Angular Distribution of Photofragments

The symmetrised central slice images of the CO ($J=40,41$) are shown in Figure 3.26. The angular distribution of both images show a slightly anisotropic distribution with respective spatial anisotropy parameters, β , of 0.78 ± 0.04 and 0.69 ± 0.04 . There is no comparison in the literature for these rotational states. Van den Brom[150] *et*

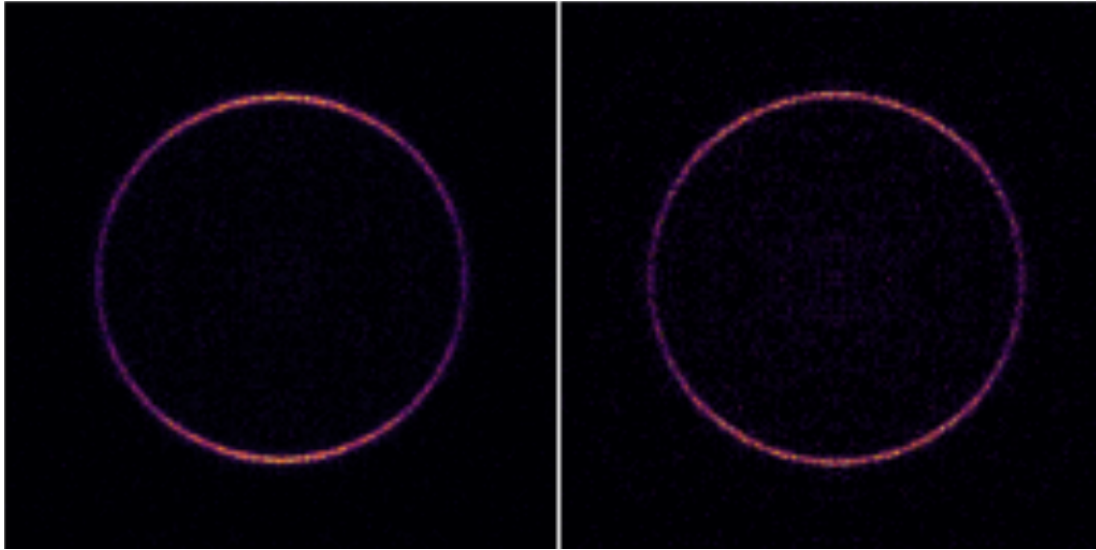


Figure 3.26: The central slice images of the two resolved CO rotational states ($J = 40, 41$).

al. report angular distribution information only down to a rotational state, $J = 43$. The anisotropy parameter for this rotational state of CO was reported as 0.61 ± 0.12 , which is comparable to those values reported here.

As previously mentioned, the velocity rings of the $S(^1D_2)$ photofragments present in Figure 3.25 are correlated with individual rotational states of the CO photofragment present in the REMPI spectrum. The velocity resolution of the central slice image in Figure 3.27 is sufficiently high that a number of rings can be resolved that could not in equivalent central slice images in Figure 3.24.

The central slice image, shown in Figure 3.27, shows the two distinct regions discussed previously, the ‘fast’ ions at large radii and the ‘slow’ ions at small radii. It is possible to differentiate many more rings, however, especially in the ‘slow’ region. This is shown more clearly in the velocity distribution in Figure 3.27. The main peak in the ‘slow’ region is distinctly two peaks which is nearly entirely resolved in the central slice image. Further, toward slower ions, smaller peaks appear down toward a radius of around 10 pixels. Notably, an inner isotropic ring (≈ 20 pixels) is observed only under PEISI conditions optimised for the S^+ Newton sphere. This feature is blurred due to out of plane contributions in the other experiments. Rings

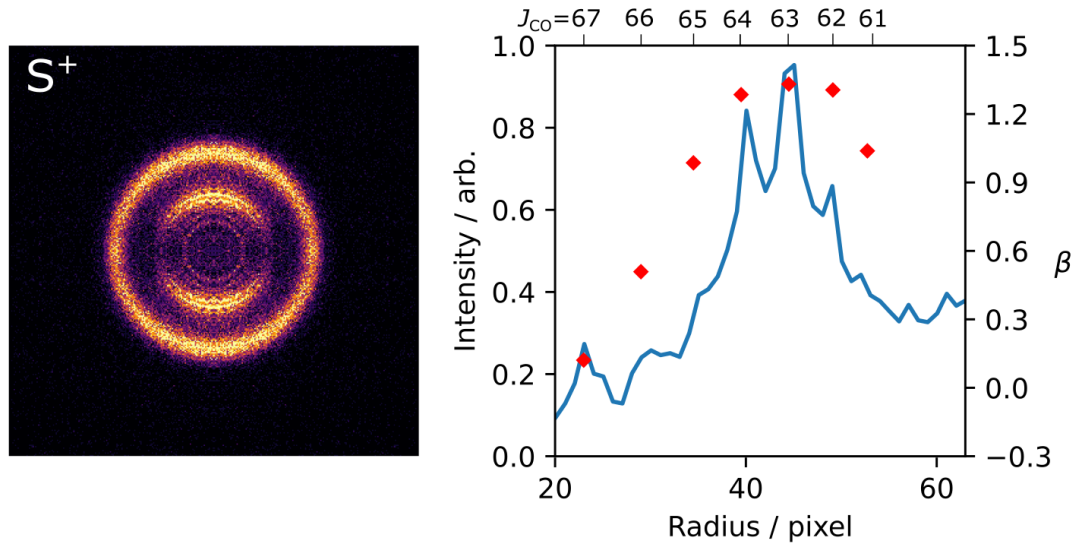


Figure 3.27: The left image shows the central slice of the sulfur photofragment under PEISI conditions. The right panel shows the resolved velocity distribution of the ‘slow’ ions with the corresponding spatial anisotropy parameters overlaid (red diamonds).

at larger radii moving out from the initial ‘slow’ peak are also visible. All distinct peaks are marked in red in the velocity distribution.

The anisotropy parameter, β , calculated for each ring is overlaid on the velocity distribution. The general trend as reported previously [118] is that the ‘fast’ ions are generally isotropic with a β parameter of around zero and the ‘slow’ ions more anisotropic with a β parameter of around 1 [118, 160]. The present work is in agreement with that general trend. The further observation that the anisotropy parameter decreases with increasing rotational state of CO (above $J = 62$) has also been reported previously [155].

The angular distributions from which the anisotropy parameters have been extracted from have also been fit to the following equation:

$$P(\theta) = \frac{1}{4\pi} [1 + \beta_2 P_2(\cos \theta) + \beta_4 P_4(\cos \theta) + \beta_6 P_6(\cos \theta)] \quad (3.23)$$

The maximum order of Legendre polynomials to appear in such an expression is given by the value $2(m+n)$ where m and n are the number of photons required to photolyse the parent molecule ($m=1$) and reach the resonant state in the photofragment ($n=2$), respectively. Thus the expansion is terminated at P_6 [166].

$J(\text{CO})$	$r(\text{S}^1\text{D}_2)/\text{px}$	This Work			Reference [166]		
		β_2	β_4	β_6	β_2	β_4	β_6
59	61	0.69	0.05	-0.07	1.32	-0.32	-0.06
60	56	0.87	-0.07	0.15	1.30	-0.37	-0.14
61	52	1.09	-0.19	0.09	1.38	0.14	0.08
62	48	1.38	-0.1	-0.15	1.29	0.01	0
63	44	1.35	-0.09	0.08	0.80	-0.14	0
64	40	1.32	-0.02	-0.1	0.24	-0.01	0.07
65	34	0.92	0.08	0.16	-0.49	-0.05	-0.06
66	29	0.67	-0.28	-0.22	-	-	-
67	23	0.17	-0.09	-0.03	-	-	-
≈ 47	78	0.32	-0.01	-0.07	0.14	0.04	0.72

Table 3.5: Extracted laboratory frame anisotropy parameters of the angular distribution of S^1D_2 photofragments, correlated to the rotational state of CO. Comparative work performed by Lipciuc *et al.* is also shown.

Table 3.5 shows the extracted laboratory anisotropy parameters, β_i , values for resolvable sulfur rings. The values are compared to similar photolysis experiments on hexapole selected $\text{OCS}(v_2 = 1|JM = 111)$ at around 235 nm[166]. The β_2 values are comparable, except for the $J = 65$ where the current work calculated a positive value. The values of β_i are sensitive to the photolysis wavelength[155, 166] and therefore it is not unexpected that these values differ. The higher order expansion terms in each work are less significant. Exact agreement would not be expected due to the hexapole state selection of OCS in the work performed by Lipciuc *et al.*[166]; whereas in the present work an ensemble of vibrationally excited parent molecules were photodissociated including that of the hexapole selected parent molecule.

For the ‘fast’ channel, the individual $\text{S}^1\text{D}_2 + \text{CO}(J)$ peaks are not resolved and a single velocity has been chosen to extract an angular distribution. The extracted β_2 and β_4 parameters are in good agreement with the work performed by Lipciuc *et al.* though they predict a larger β_6 value than has been extracted in the present work.

Covariance Analysis

Covariance analysis could in principle be employed to show that the rings in the sulfur image are correlated to the different rotational states of CO^+ . However,

two factors prevent this from being possible. Firstly, once the OCS has been photodissociated, each fragment requires a further three photons to be ionised. So for a given sulfur ion to be produced, the corresponding CO fragment must also be ionised which at these wavelengths is a very minor channel. Secondly, the second grounded plate in the PEISI set-up includes a grid to reduce distortion which in turn reduces the ion transmission to 60%. In this data, no covariance was observed between S^+ and CO^+ after over 80,000 shots of accumulation. In principle, after a long enough accumulation, covariance would be observed between the velocity feature of the two CO rotational states ($J = 40, 41$) also ionised at these wavelengths and the corresponding rings in the sulfur ion image.

3.6 Future Work and Conclusions

Post Extraction Inversion Slice Imaging has been shown to be a simple but effective modification to typical velocity map imaging spectrometers especially suitable for those able to employ event-based time-stamping cameras, such as PImMS2 or Tpx3Cam. Following design *in silico* the technique has been benchmarked experimentally for the well-known system of OCS. The technique has demonstrated marked improvements to velocity and slicing resolution. The central slice performance is comparable to that obtained under DC slicing. The performance of 3D imaging experiments is greatly improved.

This technique is currently only applicable to ions within a small m/z ratio range. This is due to the single electric field that is applied — ions that are not in the pulsed region when the pulse is applied are repelled and not detected. However, for many photodissociation experiments this would not present a problem. Further solutions to this problem are to introduce double PEDAs[62] or time-variant PEDAs[63] to allow for the inversion of Newton spheres of ions with a large difference in m/z .

Further examples of the applicability of this method will be shown in the following Chapter. The greatly enhanced velocity and slicing resolution in comparison with the ubiquitous DC slicing method is very encouraging and leads the way for further improvements. The technique could easily be extended to three-dimensional

covariance where the whole Newton sphere of ions can be properly transformed into a central reference frame. The technique could be incorporated into bimolecular scattering experiments which often have strongly anisotropic ion distributions[167–169]. This method could vastly improve the resolution of these distributions.

4

Spherical Harmonic Expansion Projection of Experimental Ion Images

4.1 Introduction

This Chapter will present a method of describing the spatial distribution of photofragments by expressing experimentally obtained VMI images as an expansion of the spherical harmonics. For an introduction to the spherical harmonics, a full discussion of the spherical harmonic expansion, and an investigation into simulated experimental data relevant to this Chapter, refer to Appendix A.

The angular distribution of photofragments, $P(\theta, \phi)$, can be written as:

$$P(\theta, \phi) = \sum_{k=0}^{\infty} \sum_{q=-k}^{+k} m_{kq} C_k^q(\theta, \phi) \quad (4.1)$$

where θ and ϕ are the polar and azimuthal angles, $C_k^q(\theta, \phi)$ are the modified spherical harmonics, k and q are the rank and projection of the spherical harmonic, m_{kq} are the weightings for each spherical harmonic and fully describe the distribution. These coefficients are known as the polarisation moments[15]. The polarisation moments, m_{kq} , can be calculated by evaluating the following integrals:

$$m_{kq} = \frac{2k+1}{4\pi} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} P(\theta, \phi) C_k^{q*}(\theta, \phi) \sin \theta d\phi d\theta \quad (4.2)$$

The coefficients, m_{kq} , are, in general, complex but can be transformed into real polarisation parameters, $m_{q\pm}^{\{k\}}$, by using Hertol-Stoll normalisation[170]. These parameters infer direct physical dynamical meanings of the full spatial distribution.

4.1.1 Photofragment Spatial Distribution Extraction

A number of approaches have been used to extract photofragment spatial distributions and hence the angular and velocity information from VMI experiments. The earliest approach employs the inverse Abel transform[123] to directly invert the recorded projected image to obtain the full three-dimensional velocity distribution. From this, the angular distribution can be fully extracted. Many sophisticated algorithms exist that perform the inverse Abel transform using different methods, such as the Fourier-Hankel transform[130], onion-peeling algorithm[127], polar basis function expansion[129] (pBASEX). Some of these techniques are described in more detail in Chapter 2. One drawback of implementing the inverse Abel transform is that the technique requires an axis of symmetry in the photofragment spatial distribution in order to be performed validly. This prerequisite is not always met in imaging experiments. Further, the resulting reconstructed images can have a reduced signal-to-noise ratio and the velocity resolution can be compromised.

A different approach employs a forward convolution fitting of the images whereby images are simulated based upon a scattering distribution[162, 171–174]. The simulated scattering distributions are then compared to experimentally measured scattering distributions to find the best-fitting initial image. Another method introduced by Bass *et al.*[175] analyses the Fourier moments of images measured in different experimental geometries.

Slice imaging[131–133, 176] made advancements in extracting the photofragment spatial distribution. This technique was discussed in detail in the previous Chapter and involves stretching the photofragment cloud along the time-of-flight axis and subsequently recording the 2D slice of the photofragment spatial distribution parallel to the imaging detector. General expressions for the photofragment spatial distribution (these can be found in Reference [15]) are greatly simplified when

considering this central slice. Experiments can be performed using photolysis light polarised along different axes and resulting central slice image subtractions can be written explicitly.

The implementation of PEISI allows for a highly resolved three-dimensional velocity distribution to be extracted directly. The experimentally determined three-dimensional velocity distribution,

$P(v_x, v_y, v_z)$, can thus be extracted from VMI images. The three-dimensional velocity distribution is related to the spatial distribution of photofragments through:

$$P(v, \theta, \phi) \sin \theta \, d\theta \, d\phi = P(v_x, v_y, v_z) \, dv_x \, dv_y \, dv_z \quad (4.3)$$

By substituting Equation (4.3) into the integrals in Equation (4.2) and evaluating, the coefficients m_{kq} can be directly calculated.

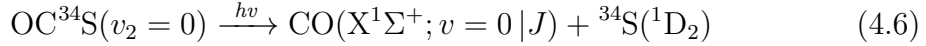
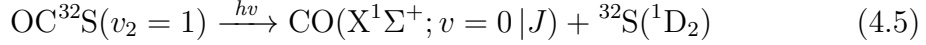
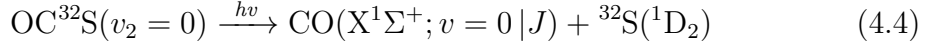
The polarisation coefficients of the angular distribution are also calculated by fitting the experimentally extracted angular distribution, $P(\theta, \phi)$ to Equation (4.1) (for $k \leq 2$) using a least-square curve-fitting algorithm. The spherical harmonic fitting (SHF) method does not give exact coefficients unlike the spherical harmonic expansion (SHE), however, the method could be useful for data where the entire Newton sphere cannot be used (and the expansion method is no longer valid).

By measuring the three-dimensional photofragment velocity distribution with sufficiently high resolution at the detector, it is therefore possible to extract the coefficients by expanding the image as a sum of spherical harmonics. This Chapter will investigate the spherical harmonic expansion of experimental VMI images of CO photofragments recorded under PEISI conditions and subsequently extract all dynamical information.

4.2 Experimental Results

The experimental set-up employed in the experiments discussed in this Chapter was discussed in detail in Chapter 3. At a given UV wavelength, more than one CO photofragments are ionised and detected resulting in multiple Newton spheres

comprising the total ion distribution. As discussed in Chapter 3, CO photofragments in a given rotational state, J derive from different parent molecules:



The PImMS data must be processed before a three-dimensional velocity distribution can be extracted. Firstly, the PImMS sensor records the ion coordinates at the detector and not the initial velocities. The relation between these quantities is discussed in Appendix A and determined through Simion simulations[142]. Secondly, as discussed in Chapter 3, a consequence of PEISI is the differential detection efficiency of ions throughout the Newton sphere which results in ions being detected undemocratically, thus affecting the extracted spatial distribution. Lastly, the distributions of CO photofragments, (in Equations (4.4), (4.5), and (4.6)) are closely separated in velocity and therefore the data must be processed such that the Newton spheres can be resolved. The CO photofragments from Equation (4.4) and (4.5) have nearly identical velocities ($v_1/v_2 = 1.014$) and cannot be resolved, while the CO photofragment from Equation (4.6) can be resolved. This section will outline the necessary steps taken to achieve this. The CO photofragments arising from isotopic OC^{34}S will be henceforth ignored.

4.2.1 Data Manipulation

The initial velocity distribution of CO photofragments can be extracted from the recorded PImMS dataset by relating each detector measurement to an initial velocity component. A relation determined from simulations performed by Simion 8.0[142] was used to transform these coordinates into initial velocity components, v_i and thence a PAD in θ and ϕ , as discussed in Appendix A

The varying detection efficiency with time-of-flight, discussed in Chapter 3, derives from the kinetic energy dependent detection efficiency of ions impinging at an MCP detector. To account for this, a ToF-dependent weighting, $\eta(t)$ was

calculated and assigned to each PImMS timebin. This term is subsequently included in the Integrals in Equation (4.2):

$$m_{kq} = \frac{2k+1}{4\pi} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \eta(t) f(\theta, \phi) C_k^{q*}(\theta, \phi) \sin \theta \, d\phi \, d\theta \quad (4.7)$$

The multiple velocity features in the PImMS images have similar velocities and are barely resolved. The separate velocity features can be resolved throughout most of the PImMS images. For this reason, thin circular slices of the desired velocity feature in each PImMS image were used to reduce the PImMS data such that the velocity distribution consisted of only the intended photofragment distribution. This reduces the statistics used for the spherical harmonic expansion but will ensure that the distribution is not contaminated by the close-lying Newton spheres. In Appendix A, it was shown how small errors in the v_i component are amplified in the v component and it is therefore essential to use only ion events that belong to a specific Newton sphere in spherical harmonic expansions.

4.2.2 Low Rotational State CO Photofragments

The CO($J = 48$) photofragment was produced and detected at wavelengths of around 230 nm. The detector recorded the x , y -, and t - coordinates of the ion events. These ion events were subsequently centroided in time and space to increase the resolution of each ion event. These were converted into velocity coordinates to extract an angular distribution, as discussed in Appendix A.

The crushed image, central slice image, and the three-dimensional image as recorded by PImMS2 are shown in Figure 4.1. Two features are observed in the central slice attributed to the CO photofragments arising from Equations (4.4) and (4.6). The three-dimensional image plots the intensity for each (x, y, t) coordinate. This visualises the Newton Sphere of CO photofragments as it is recorded by PImMS. The decrease in intensity with increasing timebin is discussed in Chapter 3, arising from the differential detection efficiency of ions[138, 139].

The real polarisation parameters, calculated from the spherical harmonic expansion and the fitting process are displayed in Table 4.1 with comparisons

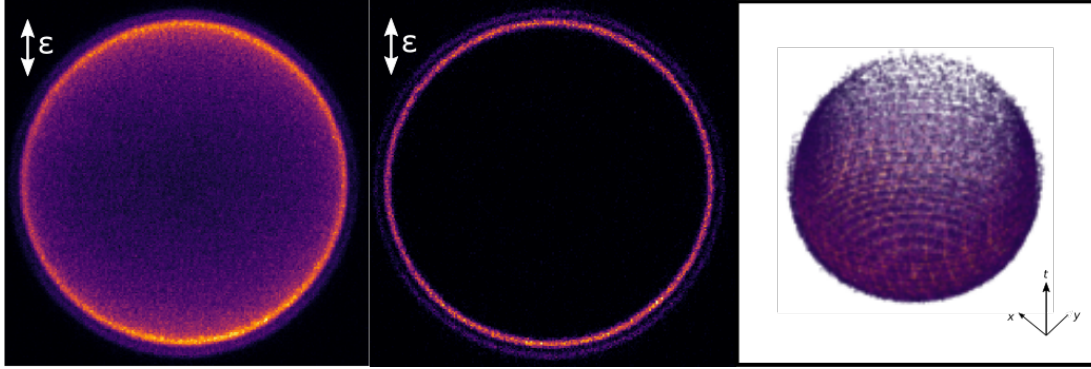


Figure 4.1: Experimentally recorded PImMS2 data. Left: 2D crushed image of the three-dimensional velocity distribution. This image can be used to reconstruct the central slice using an inverse Abel transform. Middle: central slice image recorded by PImMS. This central slice contains the same information as the reconstructed central slice attainable from the inverse Abel transform. Right: three-dimensional image recorded by PImMS2 at the detector. Newton sphere is shown visually. Time-of-flight axis is marked.

to conventional VMI techniques and literature values. Firstly, the polarisation parameters, $m_{q\pm}^{\{k\}}$, extracted from the spherical harmonic expansion are in excellent agreement with those derived from central slice analysis (see Chapter 3) and the work done by van den Brom *et al.*[150]. As expected for a single photon dissociation with no alignment effects, $m_0^{\{2\}}$ ($= \frac{1}{2}\beta_2$) is the only significant contribution to the angular distribution as determined from the spherical harmonic expansion and its value of 0.15 is in excellent agreement with the central slice analysis performed in Chapter 3 (0.13 ± 0.01) and the work done by van den Brom (0.13 ± 0.02). This corresponds to a spatial anisotropy parameter, β , of 0.30 ± 0.1 and a near-isotropic cylindrically symmetric angular distribution. The values of the remaining polarisation parameters are zero or close to zero as is expected and is reassuring that the spherical harmonic expansion reproduces these results.

The value of 0.03 ± 0.05 for $m_0^{\{1\}}$ suggests that the velocity distribution is highly symmetric about the central slice. This confirms that the transformation from the PImMS dataset to the three-dimensional velocity distribution was successful. The calculated values of ≈ 0 for the $m_{q\neq 0}^{\{k\}}$ coefficients indicate the velocity distribution is highly cylindrically symmetric.

The fitted polarisation coefficients (fourth column) broadly agree with the corresponding coefficients calculated from the spherical harmonic expansion (SHE)

k	$q\pm$	$m_{q\pm}^{\{k\}}$			
		SHE	SHF	P2 CS	van den Brom[150]
0	0	1.0	1.0	1.0	1.0
1	1-	0 ± 0	0.1 ± 0.06	-	-
1	0	0.03 ± 0.05	0.05 ± 0.07	-	-
1	1+	0.03 ± 0.02	0.09 ± 0.13	-	-
2	2-	0.0 ± 0	-0.12 ± 0.08	-	-
2	1-	0.0 ± 0	0.03 ± 0.05	-	-
2	0	0.15 ± 0.05	0.19 ± 0.08	0.13 ± 0.01	0.13 ± 0.02
2	1+	0.01 ± 0.02	0.01 ± 0.06	-	-
2	2+	-0.01 ± 0.03	-0.2 ± 0.12	-	-

Table 4.1: Comparison of extracted coefficients. Each calculated set of coefficients has been normalised such that $m_0^{\{0\}} = 1$. SHE: the spherical harmonic expansion method; SHF: spherical harmonic fitting; P2 CS: analysis of central slice recorded by PImMS; van den Brom: reference work performed by van den Brom *et al.*[150].

and from conventional VMI methods (where applicable). Notably, $m_0^{\{2\}}$ has a value of 0.19 in comparison to 0.15 and 0.13 from the SHE and PImMS central slice analysis, respectively. The coefficients typically deviate from the expected value (of zero) for the coefficients, $m_{q\neq0}^{\{k\}}$. The corresponding errors for each coefficient are much larger than for the other methods. This is not surprising as fitting two dimensional data with up to nine variables is inherently a difficult problem. The values obtained from the spherical harmonic expansion are in general more reliable than those obtained from the fitting process.

A comparison of the four-dimensional image recorded by PImMS and the analogous image reconstructed from the spherical harmonic expansion is shown in Figure 4.2. The reconstructed image was created by calculating the intensity over the unit sphere according to the coefficients in Table 4.1 to approximate the initial photofragment angular distribution. This angular distribution was then projected onto the experimentally recorded velocity distribution and finally transformed into simulated detector measurements under PEISI conditions in the Oxford VMI Spectrometer, using Simion 8.0[142].

The experimental four-dimensional image and the spherical harmonic expansion of the image are in excellent visual agreement. The PImMS2 data plotted are

the ion events that were used for the spherical harmonic expansion. This data was restricted in order to ensure that only data from the $v = 0$ Newton sphere of ions were included. This was particularly difficult for ion events where $\theta \approx \frac{\pi}{2}$ (top and bottom of the three-dimensional distribution) as the two Newton spheres cannot be totally resolved. This can be observed in the 4D image. There is also a varying thickness in parts of the sphere with the same polar angle (left and right of the three-dimensional distribution).

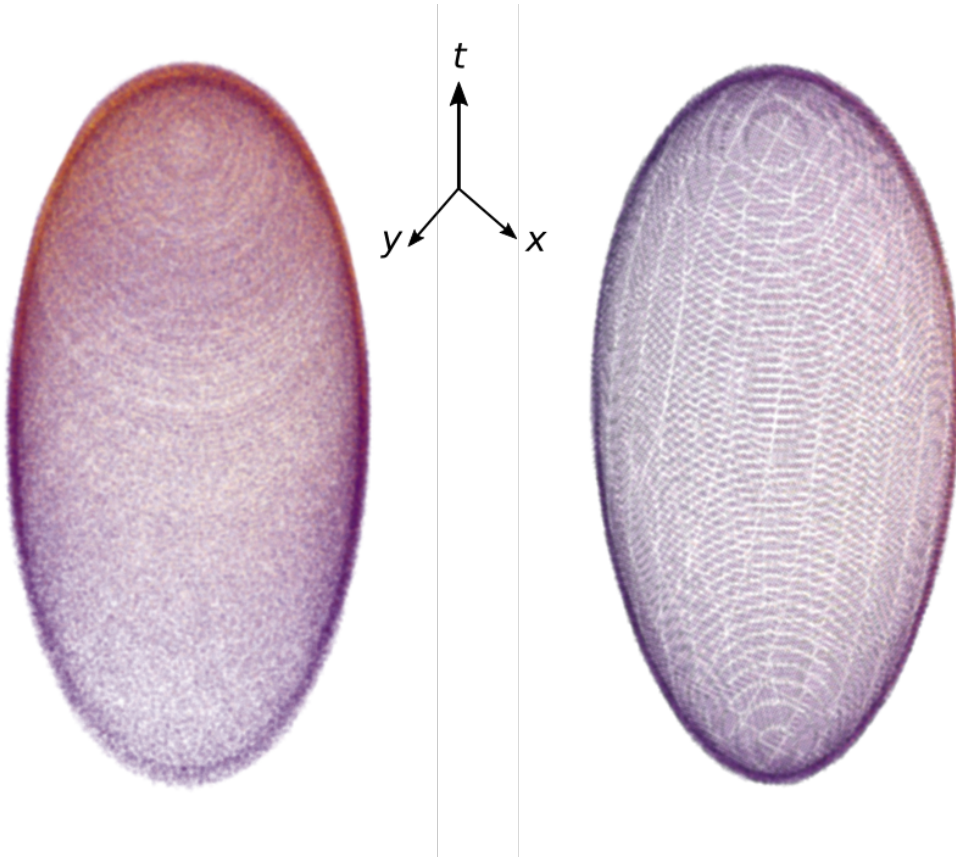


Figure 4.2: Left: the four-dimensional PImMS2 image recorded across 100 PImMS timebins. The difficulties in capturing only PImMS2 ion events corresponding to the $v = 0$ Newton sphere is evident at the time-of-flight extrema. However, the distribution is still noticeably isotropic. Right: reconstructed four-dimensional image from the spherical harmonic expansion of the image on the left. Both distributions are in excellent agreement.

4.2.3 High Rotational State CO Photofragments

The results for the $\text{CO}(J = 62)$ photofragments are detailed in this section.

k	q	$m_{q\pm}^{\{k\}}$			
		SHE	SHF	P2 CS	van den Brom[150]
0	0	1	1	1	1
1	1-	0.13 ± 0	-0.12 ± 0.01	-	-
1	0	-0.01 ± 0.01	0.03 ± 0.02	-	-
1	1+	-0.01 ± 0.0	-0.24 ± 0.03	-	-
2	2-	-0.02 ± 0.0	0.22 ± 0.02	-	-
2	1-	0.00 ± 0.01	0.06 ± 0.01	-	-
2	0	0.83 ± 0.01	0.84 ± 0.02	0.82 ± 0.02	0.81 ± 0.02
2	1+	0.02 ± 0.01	-0.02 ± 0.01	-	-
2	2+	0.25 ± 0.02	-0.36 ± 0.03	-	-

Table 4.2: Comparison of extracted coefficients. Each method has been normalised such that $m_0^{\{0\}} = 1$. SHE: the spherical harmonic expansion method; SHF: spherical harmonic fit method; P2 CS: analysis of PImMS2 central slice; van den Brom: reference work performed by van den Brom *et al.*.

Table 4.2 summarises the real polarisation parameters obtained from the various analyses of the CO photofragments borne from the photodissociation of OCS parent molecules in the ground vibrational state.

The only significant contribution to the angular distribution arises from the $m_0^{\{2\}}$ coefficient. The values of 0.83 ± 0.01 and 0.84 ± 0.02 calculated respectively by the SHE and the fitting, correspond to a strongly anisotropic distribution.

Both the spherical harmonic expansion and spherical harmonic fitting methods calculate a non-zero coefficient for $m_{2+}^{\{2\}}$ and $m_{1-}^{\{1\}}$. These would be expected to be zero for a photodissociation such as this one. These coefficients suggest that there is a region of greater intensity in the PAD for ϕ angles $0 \leq \phi \leq \frac{\pi}{2}$ and $\frac{3\pi}{2} \leq \phi \leq 2\pi$. This is likely a result of over sampling on one side of the Newton sphere when restricting the ion events by radius to ensure that the integral contains only ions from the correct Newton sphere. This process involves analysing each PImMS image of the Newton sphere and selecting the ion events that correspond to the relevant PAD. This can be a very sensitive process and a small uncertainty in the centre of an image can result in one side of the image appearing to have a greater intensity due to a larger thickness of the Newton sphere. As the Monte-Carlo integration succeeds by performing an average of the integral many times,

an over sampled part of the Newton sphere will be reflected in the results. This is what is observed for these two coefficients.

The other coefficients are sensible *i.e.* close to zero, as expected. The coefficients obtained from the spherical harmonic fit to the distribution are more varied. The coefficients corresponding to the Legendre polynomials ($m_0^{\{k\}}$) are in excellent agreement with the corresponding expansion coefficients. The $q_{\pm}^{\{k\}}$ coefficients however are more difficult to fit due to their ϕ dependence. Even so, both the fit and the expansion results are in good agreement with each other within the error range and the central slice analysis.

A comparison of the four-dimensional image recorded by PImMS and the analogous image reconstructed from the spherical harmonic expansion is shown in Figure 4.3. The reconstructed image was created by calculating the intensity over the unit sphere according to the coefficients in Table 4.2 to approximate the initial photofragment angular distribution. The angular distribution was then projected onto the measured velocity distribution to account for the velocity resolution. The final measurements at the detector were determined by transforming the initial velocity distribution onto detector positions under PEISI conditions using the Oxford VMI Spectrometer. This transformation was determined through Simion 8.0[142].

The anisotropy in the angular distributions is evident in both images. There is a shorter ion arrival time spread in these experiments in comparison with the CO($J = 48$) photofragment data due to the higher extraction field employed. This causes the less well-resolved distribution along the ToF axis in comparison to the analogous distributions in Figure 4.1.

4.3 System with a rotated axis of polarisation

Thus far, it has been shown that the technique of spherical harmonic expansion can be used successfully to describe photofragment angular distributions. However, it has only been tested against and compared with the benchmarks achieved with conventional imaging analysis techniques.

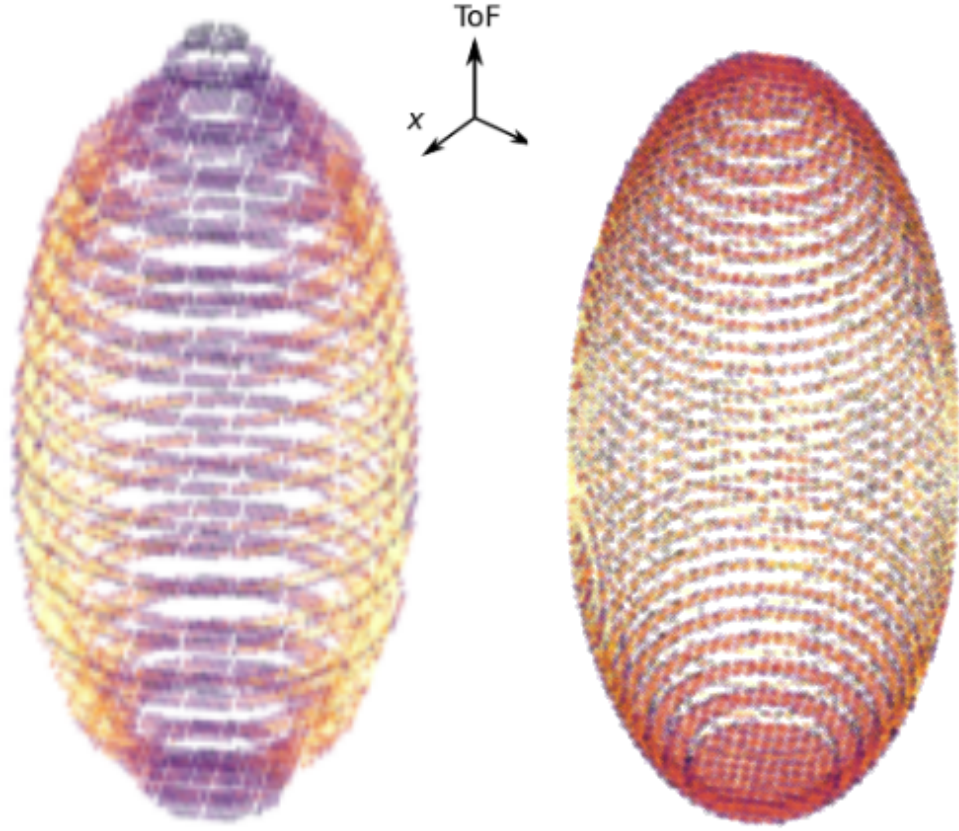


Figure 4.3: A comparison between the distribution recorded at the detector by PImMS (left) and the corresponding distribution resultant from the spherical harmonic expansion (right). See text for a more detailed explanation.

In this section, an experimental set-up will be described that deliberately breaks cylindrical symmetry so that these conventional methods are no longer valid and will not give meaningful measures of the PAD.

4.3.1 Experimental Methods

The experimental set-up is largely identical to the one described in the first section of this Chapter. However, the Rochon polariser that was used to deliver vertically polarised photolysis light to the chamber, was rotated by an angle α . The Rochon polariser alters the polarisation of light by rotating about the direction of laser propagation[89].

This has the effect of rotating the polarisation of the photolysis light about the

Z' – axis. This affects the angular distribution of nascent CO photofragments as the likelihood of OCS photodissociation depends on the angle between its trajectory and the axis of polarisation light. A cartoon of the rotation is shown in Figure 4.4. An OCS molecule is shown dissociating along the Z – axis of the photolysis light polarisation but not parallel to the laboratory frame axis. The laboratory frame axes are marked with prime notation.

As mentioned, this also breaks the cylindrical symmetry of the system. A system only possesses an axis of cylindrical symmetry if the polarisation of laser light is parallel to the detection plane. Otherwise, the detection of ions would not be symmetric upon rotation about the Z – axis. Here, as the Z – axis has been rotated deliberately, the symmetry around the laboratory Z – axis is broken and central slice analysis and methods of analysis of the 3D velocity distribution are no longer valid. In order for these to be valid the detector would have to be rotated by a complementary angle, α , which is unfeasible in the current set-up.

However, performing a spherical harmonic expansion will facilitate proper analysis of the photodissociation. This was discussed in Appendix A with the inclusion of *in silico* experiments. Briefly, detector positions were converted into initial laboratory velocities through from SIMION simulations of the spectrometer. These laboratory velocities are usually equivalent to molecular frame velocities; however the laboratory and molecular frames are no longer equivalent. A transform

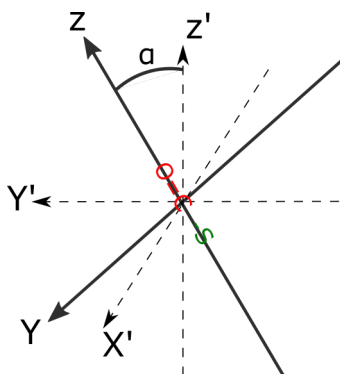


Figure 4.4: Cartoon showing how parent OCS molecules no longer photodissociate with probability according to the laboratory frame Z' – axis. A purely parallel transition in this arrangement would dissociate parallel or anti-parallel to the rotated Z – axis.

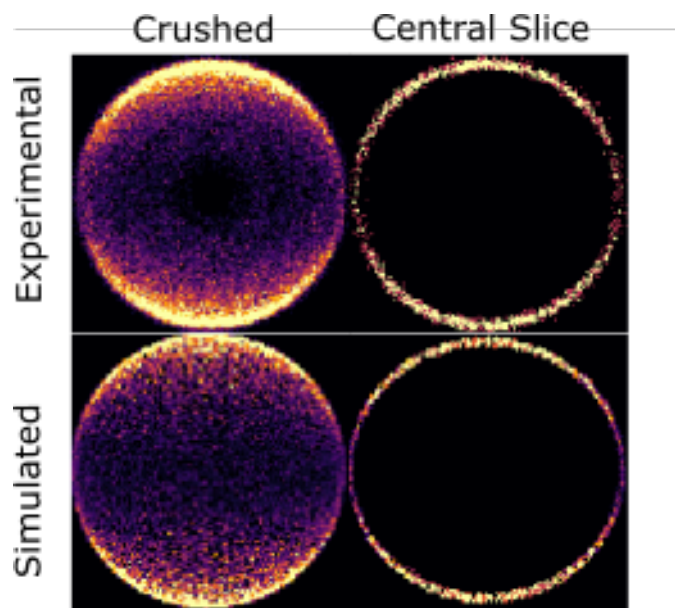


Figure 4.5: Comparison of the crushed three-dimensional image (left) and the central slice image (right) recorded experimentally (top row) and through simulations (bottom row) of $\text{CO}(J = 52)$.

between these frames must be performed in order to obtain the correct spherical coordinates necessary for the spherical harmonic expansion. This approach would not be possible in conventional VMI as more than just the central slice is required to determine the central slice in the molecular frame.

4.3.2 Experimental Results

Crushed Images and Central Slices

This section shows a comparison between the crushed and central slice images of both the experimental and simulated data of the $\text{CO}(J = 52)$ photofragment following photodissociation using photolysis light rotated by an angle, α . The top row of Figure 4.5 shows the experimentally recorded crushed and central slices of the photofragment. The bottom row shows analogous images of the simulated data.

Both the experimental and simulated crushed images are in near perfect agreement. This shows that the experimental set-up is very well understood and also that the simulation of the rotation is well understood and has been implemented

properly. The simulated and experimentally recorded central slice are also in excellent agreement.

3D slices of Newton spheres

Figure 4.6 show the images recorded by PImMS in successive timebins through the time-of-flight peak. The number of slice images and the angular distribution within each image are in excellent agreement with the corresponding simulated images in Figure A.9 in Appendix A.

Image intensity appears first on one side of the image and then after some timebins appears on the opposite side. This is a result of the anisotropic angular distribution and ions being formed predominantly along the rotated polarisation axis. The ions directed away from the detector initially arrive first under PEISI conditions on one half of the ion image. Ions on the other half of the image arrive slightly later.

Intensity increases in both halves of the image for some timebins before the ‘top’ half of the image goes through a maximum in intensity and then the ‘bottom’ half. This is shown in Figure 4.7. The ‘top’ and ‘bottom’ halves of the images are determined by splitting each slice image in two at the pixels of near zero intensity in the central images and extrapolated throughout the PAD. This proves that a conventional central slice analysis is not valid in this experimental set-up. The ‘top’ half peaks in intensity at around timebin 914 and the ‘bottom’ half correspondingly at around timebin 924. Therefore, the ‘central’ slice of the distribution does not occur at a single timebin. In fact, every θ and ϕ coordinate that constitutes part of a conventional central slice will have a range of timebins depending on the angle of rotation, α .

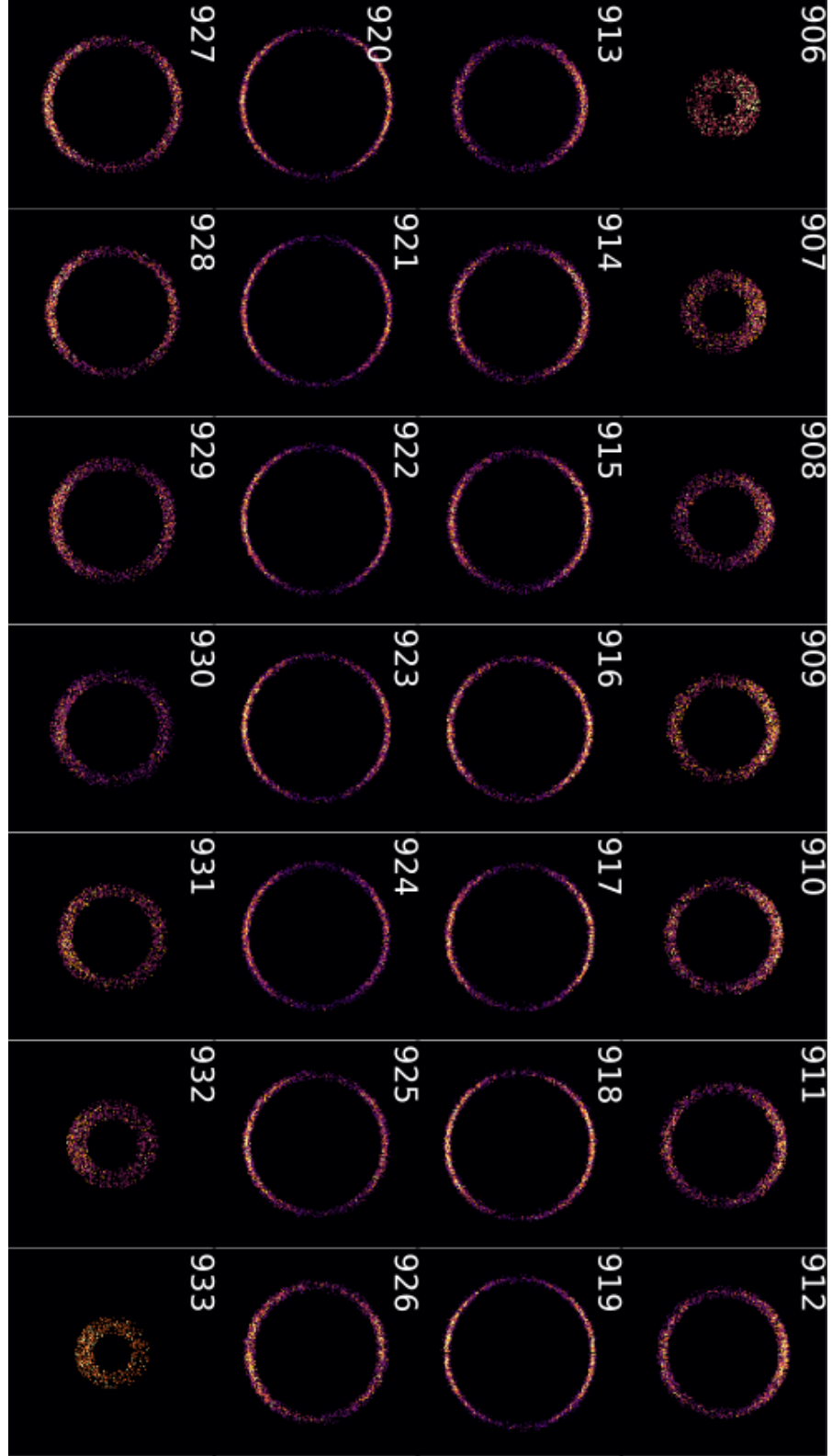


Figure 4.6: Images recorded by PImMS of the $\text{CO}(J = 52)$ photofragment as ions arrive at the detector. A PImMS image was recorded of the Newton sphere in 35 timebins and 28 are shown here. See text for more details

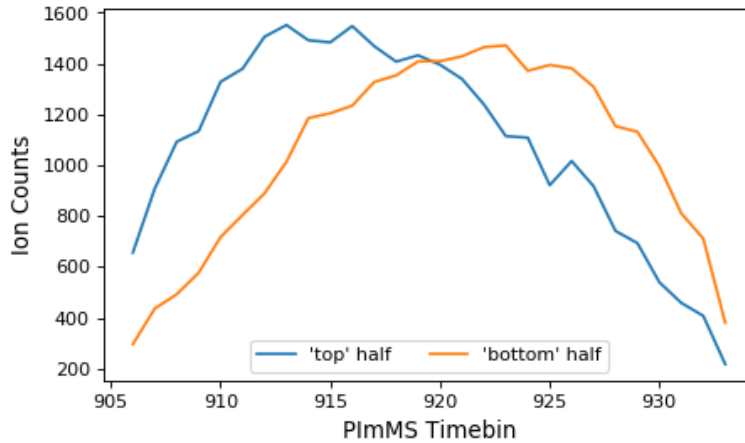


Figure 4.7: Intensity of respective halves of the total $\text{CO}(J = 52)$ photofragment as a function of timebin. See text for more details.

Approach to finding Degree of Rotation

As discussed, the axis of polarisation of light has been rotated by an angle α . This angle was approximately set to 20° , however, the exact physical value of the rotation is essential for an accurate analysis. Once, the angle, α , is satisfactorily known, the transform (detailed in Appendix A) can be performed and thence the spherical harmonic expansion. The following section will describe how an accurate value for α was extracted from the recorded data.

As mentioned briefly above, in this set-up the distribution of ions is not symmetric about the laboratory frame Z' – axis. However, the distribution still possesses an axis of cylindrical symmetry about the molecular frame Z – axis. Using this fact, the recorded PAD may be taken and rotated by a generic angle, α . This will give the initial velocity components in the molecular frame, as seen in Figure 4.4. The distributions of ions at constant z values, and therefore constant θ values, should be ϕ independent and as a result have uniform intensity. Therefore, the exact value of α (and hence the distribution of velocities in the molecular frame), can be inferred by minimising the standard deviation in the angular intensity for a given θ value. This is shown visually in Figure 4.8. A slice around the rotated Z – axis was selected. The angular intensity of this slice is shown as a function of ϕ .

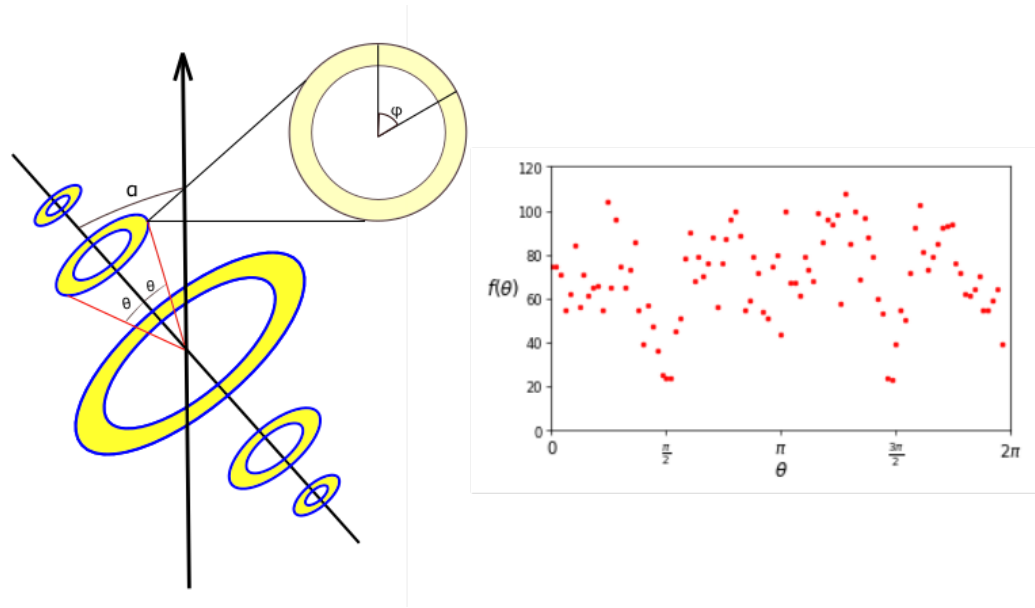


Figure 4.8: Cartoon showing the photofragment angular distribution rotated relative to the laboratory frame Z' – axis. The PAD still possesses cylindrical symmetry about the molecular frame Z – axis. Intensity profiles as a function of ϕ , shown on the right, were analysed as a function of α to minimise variation, as these should be constant due to cylindrical symmetry.

The optimisation of α is shown in Figure 4.9. There is a minimum in the value of α at around -20° , minimising where $\alpha_0 = -23.7^\circ$. The negative denotes the direction of the rotation *i.e.* which half of the distribution is rotated toward the detector and vice versa. At angles less than $\approx -30^\circ$ and higher than $\approx -5^\circ$ the intensity in ϕ deviates greatly.

The velocity components are transformed using Rodrigues' formula, detailed in Appendix A. The results are stated here:

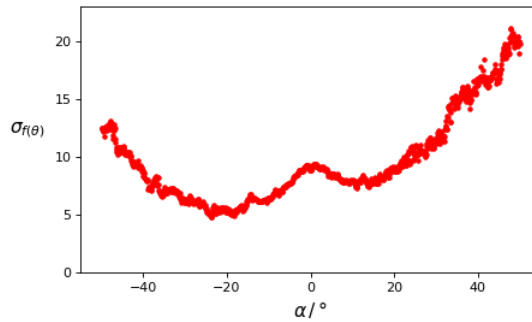


Figure 4.9: The standard deviation of the intensity profile as a function of ϕ is plotted as a function of rotated angle α .

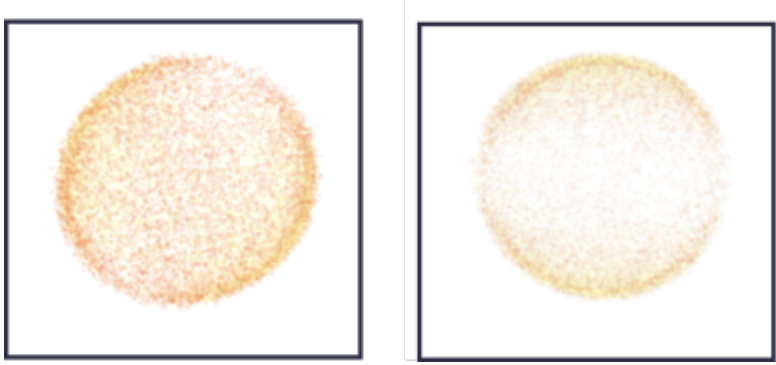


Figure 4.10: A comparison between the rotated and non-rotated three-dimensional velocity distributions. The left panel shows the velocity distribution extracted from PImMS2 data. The right panel shows the same velocity distribution transformed by the rotation of α .

$$v_x = v_{x'} \quad (4.8)$$

$$v_y = v_{y'} \cos \alpha_0 - v_{z'} \sin \alpha_0 \quad (4.9)$$

$$v_z = v_{z'} \cos \alpha_0 + v_{y'} \sin \alpha_0 \quad (4.10)$$

where the primed and unprimed notation denote the laboratory and molecular frames, respectively.

The non-rotated and the rotated three-dimensional velocity distributions are shown in Figure 4.10. The Panel on the left shows the non-rotated distribution: the distribution as recorded by PImMS after transforming to initial velocities. The anisotropic distribution can be clearly seen to be tilted toward to the left of the image. The Panel on the right shows the distribution following a rotation of α_0 . The distribution appears to be symmetric about the Z -axis. The regions of high intensity appear predominantly on the Z -axis, as is expected for a $\cos^2 \theta$ distribution. This suggests that the transformation was successful and these velocities may be converted to an angular distribution.

Spherical Harmonic Expansion

Once the velocity distribution has been rotated into the molecular frame the spherical harmonic expansion can be performed. For a proper comparison, the CO photofragment was also imaged in a crushed VMI set-up, with an unrotated

k	$q_{\pm}$	$m_{q_{\pm},\text{SHE}}^{\{k\}}$	$m_{q_{\pm},\text{CS}}^{\{k\}}$	pBASEX
0	0	1.0	1	1
1	1-	0.012 ± 0.001	-	-
1	0	0.004 ± 0.001	-	-
1	1+	-0.04 ± 0.002	-	-
2	2-	-0.007 ± 0.001	-	-
2	1-	-0.103 ± 0.002	-	-
2	0	0.716 ± 0.001	0.713 ± 0.043	0.69 ± 0.04
2	1+	0.011 ± 0.003	-	-
2	2+	0.051 ± 0.004	-	-
4	0	0.002 ± 0.003	0.056 ± 0.036	-0.014 ± 0.035

Table 4.3: Summary of the SHE extracted coefficients for the CO($J = 52$) photofragment and comparison with the β parameter extracted from fitting the angular distribution of the Abel inverted reconstruction of the central slice recorded with vertically polarised photolysis light.

polarised light. The β parameter was extracted from the inverted image. The real polarisation parameters and crushed image parameters are summarised in Table 4.3.

The angular distribution was fitted to the following model:

$$P(\theta) = 1 + \beta_2 P_2(\cos \theta) + \beta_4 P_4(\cos \theta) \quad (4.11)$$

where β_2 and β_4 contain information on the regular anisotropy parameter, β and the possible alignment of the electronic angular momentum of the states involved.

Figure 4.11 shows the inverted image of the CO photofragment and its associated angular distribution. The fit gives a β_2 and β_4 of 1.39 and -0.06 , respectively. This implies a highly anisotropic distribution with little contribution due to alignment. These are in excellent comparison with the corresponding coefficients calculated from the spherical harmonic expansion of 1.42 and -0.03 . The observed values for β are slightly lower than the literature value of 1.65 reported by van den Brom *et al.*[150]. In their experiments, OCS molecules in the ($v_2 = 0 | JM = 10$) ro-vibrational state were state selected using a hexapole and a perfect agreement is not expected. The coefficients where $q \neq 0$ are mostly close to zero, as is expected for a cylindrically symmetric PAD. The exception to this is the $m_{1-}^{\{2\}}$ coefficient that has a value of -0.103 ± 0.002 . This is likely a result of the data selection process where thin

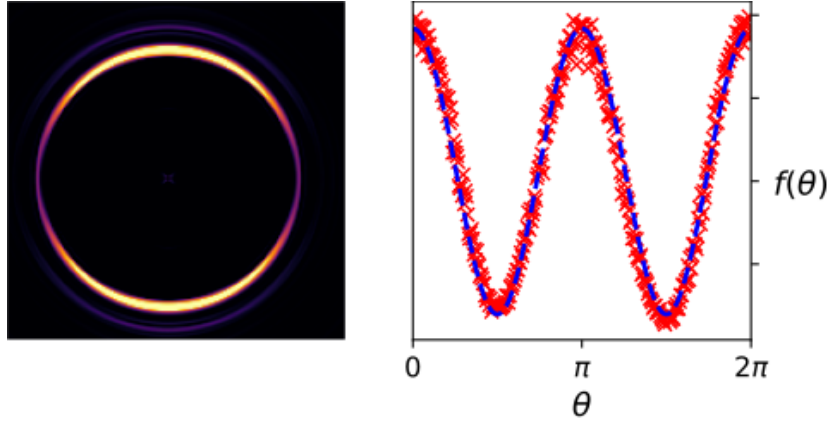


Figure 4.11: Left: the reconstructed central slice of the CO($J = 52$) photofragment following an inverse Abel transform of the crushed image. Right: the angular distribution for the $v = 0$ photofragment is shown with the associated fit to Equation 4.11

circular slices of each PImMS image were used to reduce the dataset. If one side of the image is slightly thicker there will be an asymmetry in the intensity. This asymmetry would result in a non-zero coefficient.

Effect of Rotation angle

This section measures how the rotation angle, α , affects the spherical harmonic expansion and the calculated real polarisation parameters. The recorded PImMS distribution was rotated by a different angle, α , and the coefficients were calculated once more. The results are shown in Figure 4.12.

As all the coefficients are normalised to the monopole, it is expected that $m_0^{\{0\}}$ has a value of 1 and is invariant upon changing the angle of rotation, α . This is effectively because the size of the distribution is unchanging with rotation so the scaling term is constant. The polarisation moments, $m_{q\pm}^{\{1\}}$ are very close to zero and also reasonably constant as α is changed. This is because the dipolar terms broadly describe how the distribution varies along the time-of-flight axis. However, $m_0^{\{2\}}$, $m_{1-}^{\{2\}}$ and $m_{2+}^{\{2\}}$ are all highly dependent on the angle of rotation. In this way, the rotation can be used as an alternate way to determine α as the $m_{q\neq 0}^{\{k\}}$ coefficients should equal zero for a cylindrically symmetric distribution. In addition to the method of determining α outlined earlier. The value of α that minimises $m_{1-}^{\{2\}}$ and $m_{2+}^{\{2\}}$ (to zero) in Figure 4.12 is in good agreement to that found earlier

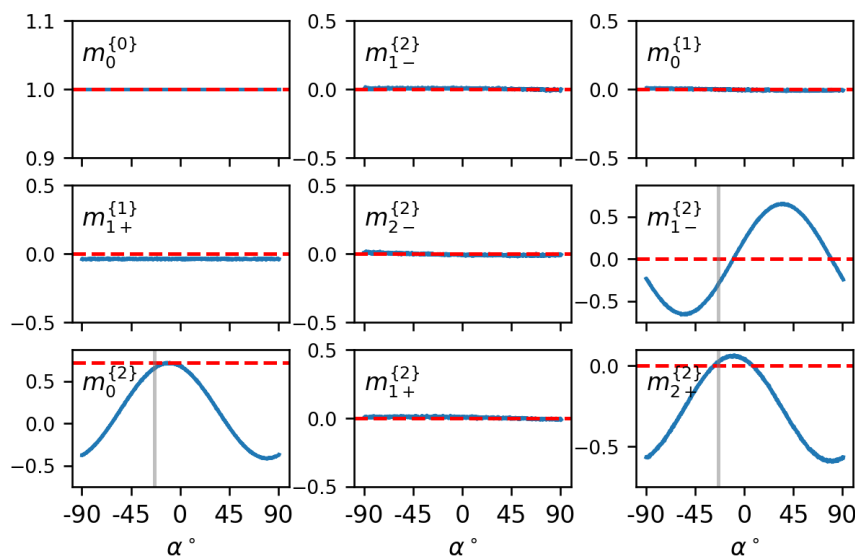


Figure 4.12: Real polarisation parameters, $m_{q\pm}^{(k)}$, measured as a function of rotation angle, α are shown as blue solid lines. Red dashed lines represent the calculated real polarisation coefficients (Table 4.3) and grey solid lines is the previously calculated rotation angle, α_0 . See text for more details.

in the Chapter ($\alpha_0 = -23.7^\circ$). For the dependent coefficients the calculated (or expected) values are indicated with a dashed, horizontal line and the optimised α is shown with a dashed, vertical line. For $m_0^{(2)}$ and $m_{2+}^{(2)}$, the α -dependent curve aligns with the expected or calculated values for the coefficients. This indicates that the rotation angle has been determined accurately. For the $m_{1-}^{(2)}$ coefficient, the value is slightly less than expected at the optimised rotation angle, as discussed earlier, this is due to the data selection process.

4.4 Conclusion

This Chapter has built on the developments of the previous work in Appendix A to show that spherical harmonic expansion analysis is a viable option that can be applied to experimental conditions. This can be a very powerful technique to elucidate reaction dynamics where multiple facets contribute to a photofragment angular distribution. Such PADs are very difficult to study as a result of the lack of high-resolution three-dimensional imaging. The capability of 3D imaging with

the advent of CMOS cameras, such as PImMS, in conjunction with the newly employed PEISI technique allows a sufficiently well-resolved velocity distribution to be used to perform a spherical harmonic expansion.

Here, an unprecedented three-dimensional velocity distribution of CO^+ ions, formed following a one-colour photodissociation of OCS and subsequent (2+1) REMPI scheme, was recorded by PImMS2 at UV wavelengths around 230 nm. The velocity distribution was converted into an angular distribution through spherical coordinate relations. This distribution was expanded as a multipolar expansion as detailed in Appendix A. The results of this were compared favourably to the crushed data and in excellent agreement with the literature. To further test the technique, cylindrical symmetry was deliberately broken by rotating the axis of polarisation of the photolysis light. In this instance, it is impossible to extract valid dynamical information on the PAD. Inverse Abel transforms are not valid in these circumstances as the algorithms rely on the pre-requisite of cylindrical symmetry. Similarly, anisotropy parameters can no longer be extracted through analysis of the ‘central slice’ in this case. However, by determining the angle of rotation, the distribution can be rotated into the molecular frame and the spherical harmonic expansion may be validly performed. This was shown to work excellently, agreeing with the Abel transform of the crushed corresponding photofragment angular distribution resulting from cylindrically symmetric conditions.

Spherical harmonic fitting has also been used to determine the real polarisation parameters. Though this method qualitatively worked well, its accuracy was markedly worse than the spherical harmonic expansion. This is unsurprising as the process relies on a two-dimensional fitting which is inherently difficult and the SHE exploits the properties of the spherical harmonics to simplify the problem.

In summary, this technique displays the full benefit of PImMS2 and other CMOS time-stamping cameras in capturing a three-dimensional distribution of the photofragment angular distribution. In combination with PEISI, the number of slices of the Newton sphere that PImMS2 is able to record is increased greatly, allowing for the first time a technique of this kind to be fully utilised.

4.5 Future Work

It would be useful to validate this method and this work by investigating the orbital angular momentum polarisation benchmark in a molecule such as molecular chlorine. The atomic angular distributions are well-known and have no cylindrical symmetry. It would be a true test of the power of this technique in combination with PImMS and PEISI imaging[15, 172].

It would also be of great advantage to extend this method to extract velocity-dependent parameters, $m_{q\pm}^{\{k\}}(v)$. A model system with nested Newton spheres well-separated in velocity would be an ideal candidate to achieve this.

Future work on this subject will also focus on applying these methods to Coulomb Explosion Imaging. Ionising through Coulomb explosions, often causes highly anisotropic angular distributions and ions of the same m/z ratio with multiple pathways, each with a corresponding unique kinetic energy. Spherical harmonic expansion of 3D images has been shown to be an advantageous technique to studying these nested Newton sphere systems.

Increased timing resolution will always improve the performance of this technique as greater timing resolution results in the higher the fidelity of measured spherical coordinates. Greater timing resolution could be achieved through the use of other CMOS cameras such as Timepix3Cam[49, 52, 65].

Another approach to increase the timing resolution is by fitting an analogue-to-digital current (ADC) readout to the back of the MCP on the detector. This would convert the current of impinging ions at the detector into a digital signal. Theoretically, the MCPs have a timing resolution of < 1 ns. The digital signal can be coupled to the cluster size of ion events identified from the clustering algorithm of pixel events recorded by the PImMS camera. If the condition that digital signal scales linearly with cluster size is met (unpublished work, Felix Allum), then PImMS clusters can be correlated to ADC signals and thereafter reassigned temporally according to the increased resolution of the ADC readout. Again, this method would greatly increase the resolution of these experiments. Similar approaches have been successful by Li and coworkers[177] and Suits and coworkers[178].

5

Principles of Coulomb Explosion Imaging

Coulomb Explosion Imaging (CEI) is a technique that utilises the photoinduced Coulomb explosion of a molecule to record the photofragment ion momenta under VMI conditions. In this Chapter, the concept of a Coulomb explosion and CEI will be introduced. A discussion of some ionisation methods that can induce Coulomb explosions in molecules will also be presented, with a particular focus on those that feature in the following Chapters. These include strong-field ionisation, inner-shell ionisation, and non-resonant multiphoton ionisation.

Finally, as the CEI experiments presented in this thesis were undertaken at high count rates, the relevance of covariance analysis will be discussed. After which, an explanation of this statistical method will be given and how it can be applied to PImMS data in these experiments.

5.1 Background

A key goal of femtochemistry[28, 30] is to obtain structural information on a chemical system as it evolves temporally. This is a very powerful prospect as it would allow for the accumulation of a ‘molecular movie’ where detailed structural changes can be observed as the reaction unfurls. This ambition is not without its challenges. Firstly, it is difficult to find a method of probing the structure that does not simultaneously

perturb the structure in some way. Further, determining the structure requires a full description of the coordinates of each atom. Therefore, the probe method will have to provide an information-rich dataset in order to fully describe the structure.

Coulomb explosion imaging is a technique that can extract such structural information from a system on an ultrashort timescale. A Coulomb explosion is a rapid ionisation whereby several electrons are removed from an isolated molecule, resulting in the formation of an unstable cation. The resultant mutual electrostatic repulsion of charged fragments far outweighs the residual binding energies between fragments and a rapid dissociation into fragment ions occurs.

The first Coulomb explosion (CE) experiments investigated simple molecules, such as H_2^+ and HeH^+ , through a collision of a fast ($\sim \text{MeV}$) molecular beam, with a thin foil[179]. The interaction time between the high-energy molecule beam and the foil was prompt enough ($\sim 10^{-15} \text{ s}$) that the nuclear motion of the target molecule was assumed to be fixed and structural information could be inferred from the detection. Vager *et al.*[13, 180] used this technique to identify the stereochemistry of methane ions. The final velocity vectors of the carbon and hydrogen ions were sufficient to describe fully the initial geometry of the methane ion.

The advancements in laser physics in recent years has greatly enhanced the potential for light-induced Coulomb explosions. Particularly, the development of high-intensity, ultrashort ($\sim 10^{-15} \text{ s}$) lasers allow for conventional VMI methods to exploit Coulomb explosions in order to probe target molecules, without relying on high-energy molecular beams[14, 181–185]. In such experiments, a laser pulse induces a Coulomb explosion in a molecule and the ion velocities are measured and subsequently used to extract the desired structural information.

The development of a ‘molecular movie’ is often sought as the ultimate goal for this imaging method. This can be achieved *via* time-resolved pump-probe Coulomb explosion imaging. This is illustrated in Figure 5.1. Two laser pulses are employed: a pump pulse excites the target molecule from its ground state to an excited state surface; and a probe pulse induces a CE in the excited molecule. The time-delay, Δt , between the pump and probe pulses allows the pumped wave packet to evolve

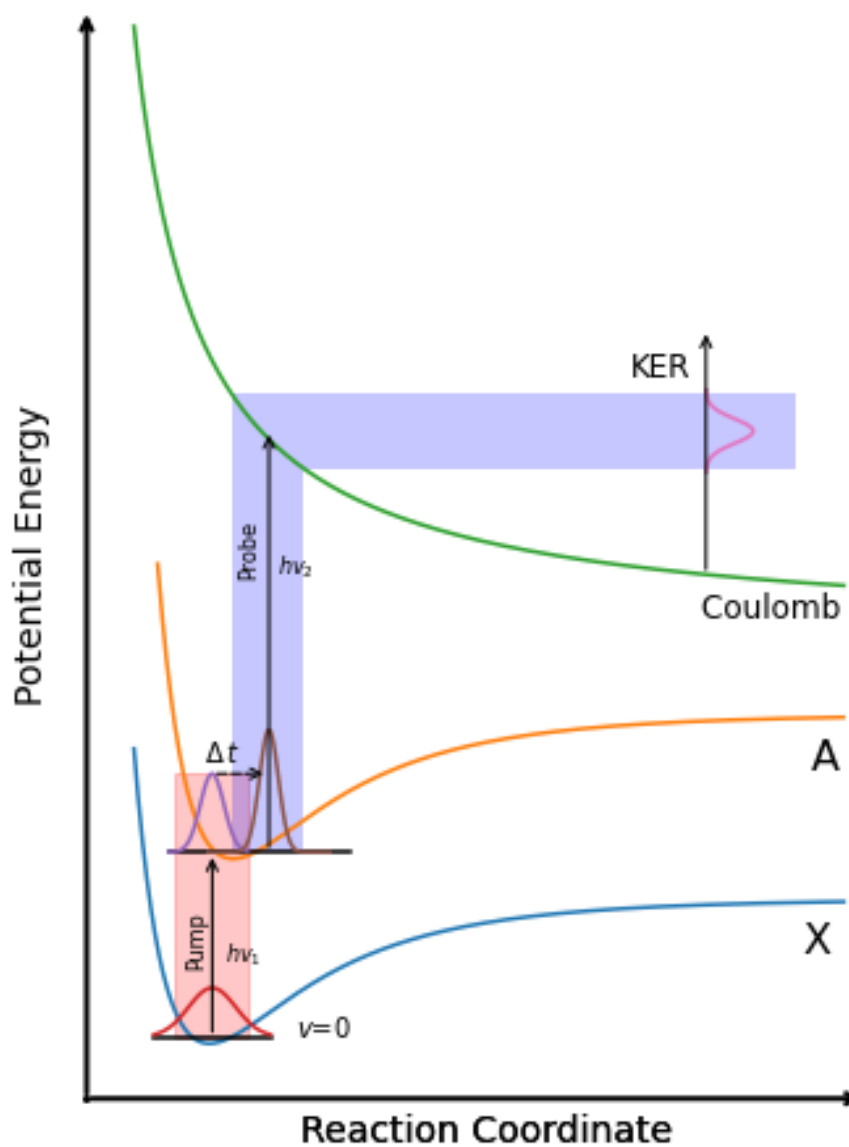


Figure 5.1: Reaction scheme illustrating the principles of a pump-probe CEI experiment. The initial ground-state wave-function is pumped onto an excited potential surface. The system is allowed to evolve for a delay, Δt . After which the probe pulse rapidly ionises the evolved intermediate state to form highly charged molecular ions on the Coulomb potential energy surface. The electrostatic repulsion of ions yields fragment ions with final velocities that are characteristic of the molecular structure at the time of the probe pulse.

on the excited surface. The probe pulse induces a Coulomb explosion by rapidly dissociating into fragment ions and subsequently transfers the wave packet onto a Coulomb surface, where the ion velocities can be recorded through for instance velocity-map imaging. By performing a series of Coulomb explosion experiments at a number of pump-probe delays, the structural changes that occur can be measured.

5.2 Intense Laser Field Ionisation

Strong-field ionisation is the term for the method of ionisation whereby the intensity of the electric field significantly affects the potential experienced by a bound electron even if the photon energy is less than the ionisation potential. At typical electric field intensities of $\sim 10^{14} \text{ W cm}^{-2}$, the electric field generated is comparable to that of the electrostatic attraction between the electrons and nuclei in the target molecule and strong-field effects are expected[186, 187].

When the photon energy is considerably smaller than the ionisation potential, ionisation may proceed in one of three ways. Firstly, if the laser intensity is not relatively strong, ionisation can occur *via* multiple photon absorption where the prompt absorption of photons allows the target molecule to reach the ionisation energy. Secondly, with increasing laser field intensity, the potential experienced by electrons is perturbed such that the barrier for ionisation is reduced sufficiently and electrons are likely to tunnel into the continuum and ionise the molecule. At sufficiently high field strengths, the ionisation barrier is reduced to below the valence electron binding energy, resulting in over-the-barrier ionisation. These regimes are depicted in Figure 5.2.

An approximate expression to determine the dominant ionisation regime in a system is given by the Keldysh parameter[188]:

$$\gamma = \sqrt{\frac{I_P}{2U_P}} \quad (5.1)$$

where I_P and U_P are the field-free ionisation potential and the ponderomotive energy of the electron, defined as:

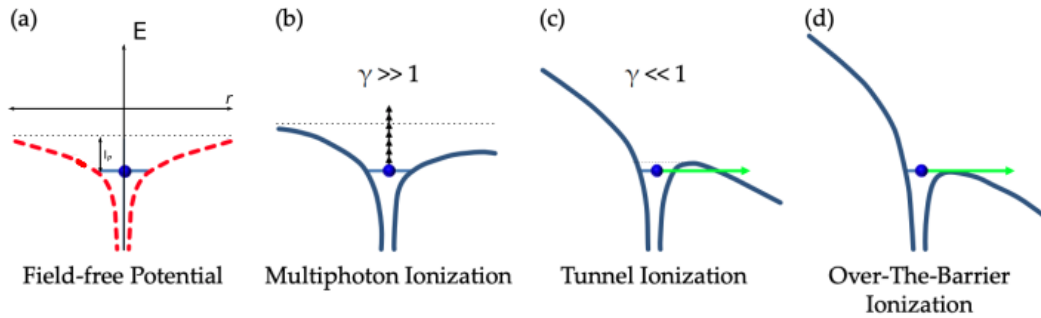


Figure 5.2: Illustration of the ionisation regimes with increasing laser intensity. (a) shows the unperturbed field-free potential, (b-d) show the potential experienced by an electron with increasing electric fields resulting in multiphoton ionisation (b), tunnel ionisation (c), and over-the-barrier (d) ionisation. Figure adapted from Reference [189]

$$U_P = \frac{e^2 E_0^2}{4m_e \omega^2} \quad (5.2)$$

where E_0 and ω are the amplitude and angular frequency of the laser field, e is the elementary charge and m_e is the mass of an electron. This energy represents the average energy imparted on an electron subject to the given electric field. The value of the Keldysh parameter can indicate the nature of the ionisation of a molecule subject to an intense laser field. If the Keldysh parameter, $\gamma \gg 1$, multiphoton ionisation dominates. In these cases, either the binding energy of the electron is far greater than the electric field strength or the frequency of the oscillations of the electric field is much faster than the tunnelling rate for the electrons. For situations where $\gamma \ll 1$, strong-field ionisation dominates, leading to tunnelling or over-the-barrier ionisation.

5.3 Inner-Shell Ionisation

Inner-shell ionisation involves the removal of an electron from a core molecular orbital resulting in a core hole. The electron vacancy is promptly repopulated by a fast Auger decay or cascade, accompanied by the removal of at least one more electron to generate a multiply charged ion[190, 191]. A photon that causes inner-shell ionisation must have a photon energy that exceeds the binding energy of the core electron. In order to site-selectively ionise at a specific atom, there

Atom	Absolute Cross-section / Mb	Relative Cross-section
S	2.22	1
O	0.25	0.11
C	0.45	0.22
H	0.004	0.002

Table 5.1: Table summarising the total absorption cross-sections of all the energetically accessible atomic orbitals of the constituent atoms in thiophenone and their relative cross-sections for a photon energy of 206 eV. Data taken from Reference [113]. The unit for absorption cross-section is m^2 , measurements here are given in Mb, where 1 b (barn) is equivalent to 10^{-28} m^2 or 100 fm^2 .

should also be a dominant atomic absorption cross-section, $\sigma(\text{abs})$ relative to other molecular constituents. This is helpful as it allows for the initial charge location to be known. In this way multiple charges can be induced with a high-degree of spatial localisation at a (typically heavy) element with a large X-ray absorption cross-section[192]. This allows for charge transfer experiments to be performed where the initial charge location can be known reliably[71, 97, 193].

This will be demonstrated for the case of thiophenone, $\text{C}_4\text{H}_4\text{OS}$ [113], at a photon energy of 197 eV. Table 5.1 gives the total absorption cross-sections of the constituent atomic orbitals[113] in thiophenone at the experimentally employed photon energy of 197 eV. Absorption cross-section values from Reference [113] have been multiplied by the number of each atoms present in thiophenone to account for the increased probability of absorbing at, for instance, the carbon atom. Accounting for this there is at least a ~ 5 times greater probability of removing an electron from the sulfur atom than any other atom and ~ 3 times more likely to remove an electron from the sulfur atom than from anywhere else on the molecule.

Table 5.2 shows the calculated absorption cross-sections for the accessible atomic orbitals present in thiophenone. Atomic orbitals that are not energetically accessible at this photon energy have been omitted as these orbital electrons can not be ionised (*i.e.* $\text{S}(2s) = 224 \text{ eV}$, $\text{O}(1s) = 536 \text{ eV}$; $\text{C}(1s) = 290 \text{ eV}$). Here, it is apparent that the ionisation predominantly occurs at the $\text{S}(2p)$ orbital as the absorption cross-section for this orbital is ~ 3 times more likely than all the other accessible orbitals combined. The cross-section for the molecular orbitals (eg $\text{S}(3s)$ or $\text{C}(2p)$)

Atom	Orbital	Cross-section / Mb	Relative Cross-section
S	3s	0.126	0.06
	3p	0.100	0.05
	2p	1.995	1.0
O	2s	0.126	0.06
	2p	0.126	0.06
C	2s	0.05	0.025
	2p	0.400	0.200
H	1s	0.004	0.002

Table 5.2: Table summarising the absorption cross-sections of atomic orbitals of the constituent atoms in thiophenone and their relative cross-sections for a photon energy of 197 eV. Data taken from Reference [113].

are considerable smaller than the strongly bound S(2p) orbital. More strongly bound electrons that are not involved in molecular bonding are typically the best targets for inner-shell ionisation.

Therefore, the inner-shell ionisation generates consistently a localised hole in the S(2p) orbital. Many relaxation and Auger pathways can subsequently take place and will be discussed in more detail in the next section. Atoms that have undergone inner-shell ionisation of an electron with a binding energy of E_1 can dissipate energy and fill core holes in a number of different relaxation pathways. These relaxation pathways can either be radiative or non-radiative[194, 195].

5.3.1 Relaxation Processes

Radiative Processes

Fluorescence decay or X-ray fluorescence[195] is a typical radiative relaxation process in which an electron from a shallower orbital of binding energy E_2 fills the inner-core hole. The energy balance is carried away by a photon of energy, $E_{h\nu}$, where:

$$E_{h\nu} = E_1 - E_2 \quad (5.3)$$

In this scenario, the charge of the atom remains unchanged.

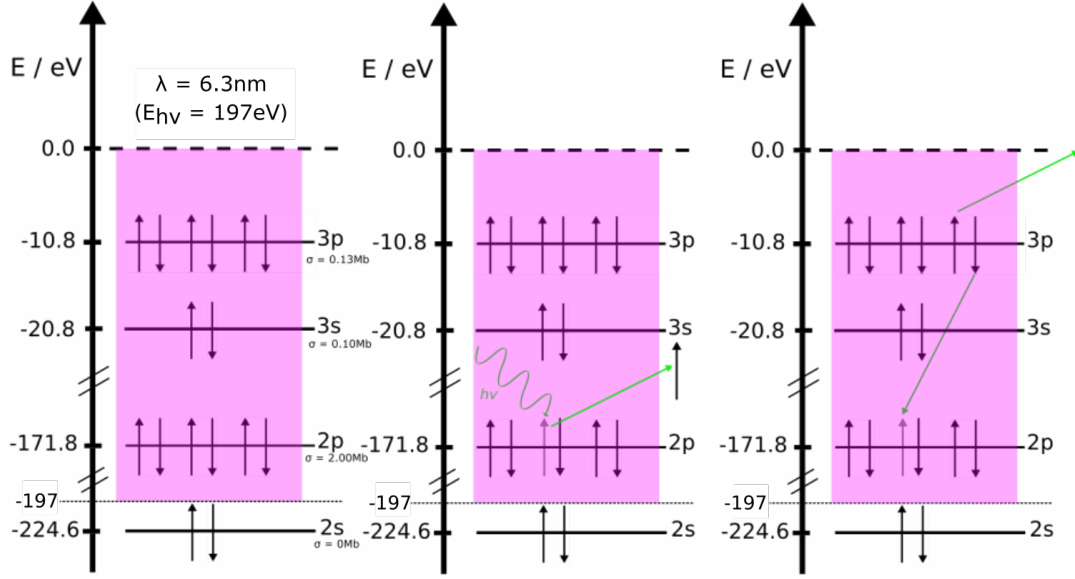


Figure 5.3: The energy scheme of the four highest occupied atomic orbitals of atomic sulfur. The binding energies of atomic sulfur are shown from Reference [113]. The left panel presents the orbitals that are energetically accessible at 197 eV shown by the pink shading. The middle panel shows the creation of a core-hole after the ejection of an electron from the 2p atomic orbital following the absorption of a 197 eV photon [190, 191]. The right panel illustrates the typical Auger decay[194, 195] mechanism that occurs following the ejection of an electron from the 2p atomic orbital of sulfur. See text for details.

Auger Decays

Alternatively, an Auger decay can occur[190]. An Auger decay is a non-radiative relaxation process whereby instead of emitting a photon, a higher-lying electron (with a binding energy, E_3), termed an Auger electron, is ejected from the atom, with an energy, E_A

$$E_A = E_1 - E_2 - E_3^* \quad (5.4)$$

where E_3^* is the binding energy of electron in the third level with a vacancy in the first level. This results in a further charge being put on the atom and electron holes in the second and third levels. This process can be repeated multiple times as the re-filled inner-core electron can be ionised by further photons thus removing many electrons from the system.

It is also possible for a radiative Auger decay to occur[196]. In this process, the simultaneous ejection of an Auger electron and a photon are emitted from the atom.

Double Auger decay processes are also possible in which two Auger electrons are ejected resulting in a trication being produced. This is always a much weaker channel than a single Auger decay but has been experimentally observed[197–199]. Some of these processes are illustrated pictorially in Figure 5.3.

Shake-related Processes

The energy of emitted photoelectrons and the number of emitted electrons can be affected through shake-related processes[200, 201]. The ionised inner-shell electron leaves rapidly such that more weakly bound electrons are not able to relax. The resultant interaction between the departing photoelectron and the remaining electrons and the subsequent collective excitation are known as shake-related processes[202–205]. Shake-off processes correspond to processes where the relaxation of weakly-bound electrons results in secondary emission. These processes are a consequence of the sudden increase in effective charge experienced by the electrons[200, 206, 207]. Shake-up processes correspond to the process whereby one or more bound electrons take energy from the departing photoelectron and are excited to bound states[201, 208–212].

The next section will outline some sources of high energy photons that are capable of inducing inner-shell ionisation.

5.3.2 XUV Lightsources

As discussed in the previous section, in order to be in the inner-shell ionisation regime, photon energies must be at least as great as the binding energies of core electrons. Typically, this condition dictates that the photons must be in the XUV part of the electromagnetic spectrum. This section will explore the three most common XUV lightsources: free-electron lasers (FELs), high-harmonic generation (HHG), and synchrotron radiation.

Free-electron Laser

Free-electron lasers (FELs) are accelerator-based lightsources that can generate [100–105] intense ($10^{12} - 10^{14}$ photons pulse⁻¹), ultrashort (2 – 300 fs) pulses in the XUV range (0.12 – 52 nm)[103, 106]. FELs can therefore provide access to the single-photon and multi-photon absorption regime.

Free-electron sources accelerate a pulse of electrons to relativistic speeds through a superconducting linear accelerator. The electrons are then passed through an undulator[108], which causes the electrons to undergo Self-Amplified Spontaneous Emission (SASE), resulting in the emission of extreme ultraviolet (XUV) photons. A more detailed discussion of the working principles of free-electron lasers was discussed in Chapter 2.

High-Harmonic Generation

In High-Harmonic Generation (HHG) a non-resonant intense laser pulse emits an electron from a target which subsequently recombines with its parent[213–220]. As the electron scatters with the parent molecule in the presence of a strong-field, the sample emits high harmonics (integer multiples) of the initial generation beam, with relatively large photon energies, ultrashort pulse widths, and coherent radiation[221]. HHG also has the advantage of being produced in a compact setting *i.e.* without the need of a linear accelerator.

Specific harmonic wavelengths can be generated using various techniques, such as metal filters[218], dielectric multilayers[222], and a XUV time-delay-compensated monochromators[221].

HHG can produce very short laser pulses (< 1 fs) however the pulse intensity is relatively low in comparison with FELs and also decreases with increasing energy.

Synchrotron Radiation

Synchrotron radiation facilities are accelerator-based light sources that can access photon energies of > 10 eV at fast repetition rates ($\sim$ MHz). Like FELs, synchrotron

radiation is the emitted radiation of an accelerated electron beam as it traverses through an undulator[223].

The photon intensities tend to be much greater than those produced in HHG, though are not in the multi-photon absorption regime. The pulse widths of synchrotron radiation is relatively long (> 50 ps) and is therefore not applicable to pump-probe femtosecond chemistry dynamic studies[223].

5.4 Covariance Analysis

FEL employed experiments typically produce many ions per laser shot ($10^2 - 10^3$ ions shot $^{-1}$). Coulomb explosion experiments induced *via* strong-field ionisation can also produce many ions per shot. These ionisation regimes correspond to a relatively high count rate and, as will be shown later, precludes coincidence analysis. However, under these conditions it is possible to employ covariance analysis[58, 59, 70, 71, 80, 121, 224–227] to find correlations in the data that cannot otherwise be gleaned from ion images or time-of-flight analysis. Covariance analysis is a statistical method that describes how a change in one measured variable may correlate with another measured variable. Mathematically, the covariance between two signals of interest X and Y was described in Equations (1.8), (1.9), and (1.10).

Covariance can be calculated between different signals in such experiments to glean ion correlations. For instance, correlations between ion time-of-flight signals using high-resolution ToF analysis or between pixel events deriving from different ions[58, 70, 71, 80, 121, 224, 225, 227–231]. These two scenarios will be discussed in more detail in the following sections.

5.4.1 Time-of-Flight Covariance

Time-of-Flight (ToF) covariance was first pioneered by Frasinski and coworkers[80] who used covariance between ion time-of-flight signals to determine correlations between ions. ToF covariance has been employed extensively since[69, 70].

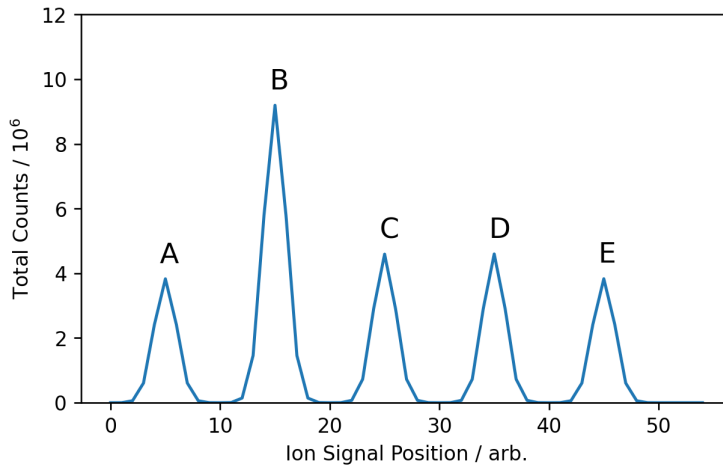
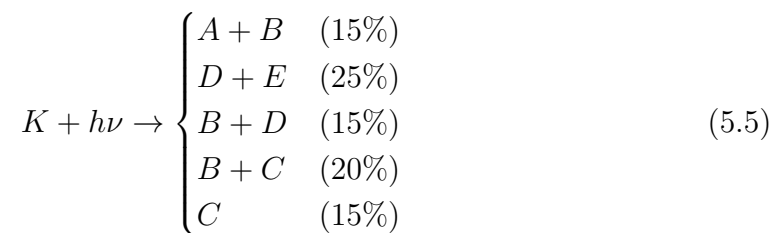


Figure 5.4: Simulated integrated one-dimensional ion signal spectrum according to reaction scheme in Equation (5.5). Spectrum obtained with an ionisation rate, $k_I = 100 \text{ shot}^{-1}$.

Simulated Time-of-Flight Covariance

A model system was used to investigate the coincidence and covariance maps with varying count rates in a simulated VMI experiment. In the simulation, a parent molecule K interacts with a photon, $h\nu$ and undergoes some photochemistry resulting in the formation of ions A, B, C, D, E in the simplistic reaction mechanism as follows:



The simulation consisted of $N_{\text{shots}} = 1 \times 10^6$ with ionisation rates, k_I of 0.01, 1, 100 shot^{-1} to simulate varying experimental count rates. An ion detection probability, η , of 0.6 was used to simulate a typical MCP detection efficiency. The simulated integrated ion signal is shown in Figure 5.4 for an ionisation rate of 100 shot^{-1} .

The simulated coincidence (left) and covariance (right) maps are shown in Figure 5.5. Ion correlations should be observed according to the reaction scheme

in Equation (5.5) *i.e.* correlations between A and B , and B and C etc. but not between for instance A and C . At low count rates (top row), the coincidence and covariance maps are essentially identical. However as the ionisation rate is increased, false correlations are observed between C and other fragments. This is because the uncorrelated contributions can not be ignored. In the respective covariance maps, these false correlations are removed and show no contamination.

Partial Time-of-Flight Covariance

For ToF covariance to be successful there should be a stable photon flux from the light source, in this case the FEL. The stochastic nature of XUV pulse generation[108] by the FLASH FEL results in a photon flux or pulse energy that fluctuates on a shot-by-shot basis. As the number of ions generated varies linearly with pulse energy, more ions are produced for FEL shots of a higher pulse energy and vice versa. The effect of this in the ToF covariance map is artificial correlations between ions appear in the covariance map. To overcome these artificial correlations, partial covariance mapping should be used. Partial covariance mapping takes into account the fluctuating pulse energy for each shot, and is calculated as:

$$\text{pCov}(X, Y) = \text{Cov}(X, Y) - \text{Corr}(X, Y) \quad (5.6)$$

where $\text{Corr}(X, Y)$ is calculated:

$$\text{Corr}(X, Y) = \frac{\text{Cov}(X, I)\text{Cov}(Y, I)}{\text{Var}(I)} \quad (5.7)$$

where $\text{pCov}(X, Y)$ is the calculated partial covariance, $\text{Cov}(X, Y)$ is the previously calculated covariance (from Equation (1.8)), and I is the fluctuating parameter for each shot as recorded by the FLASH DAQ. $\text{Var}(I)$ is the variance of the pulse energy calculated over all shots.

Figure 5.6 shows the total covariance map (left) and the partial covariance map (right) for the reaction scheme in Equation 5.5 at an ionisation rate of 10 shot^{-1} and a linear power dependence.

$$N_{\text{ions}} = Pk_I \quad (5.8)$$

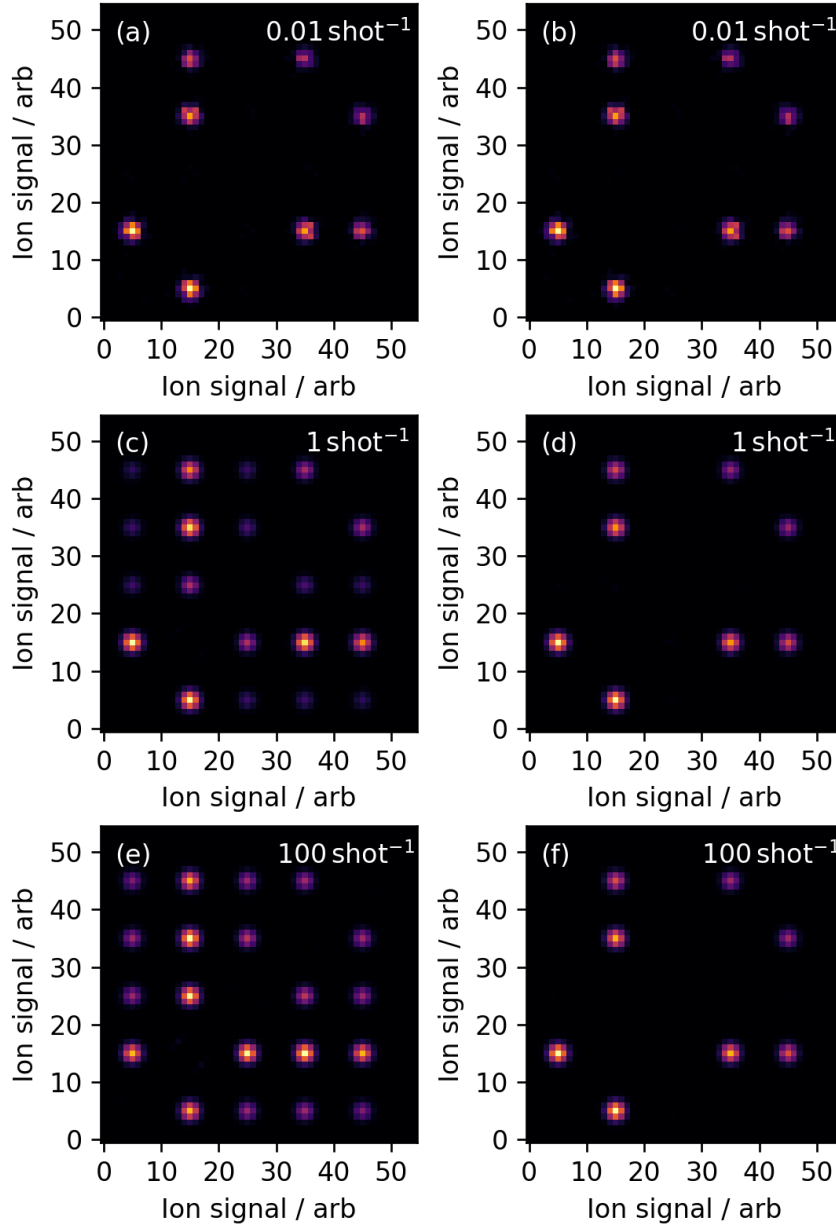


Figure 5.5: Coincidence (left) and covariance (right) maps for the simulated reaction scheme given in (5.5). Successive rows correspond to ionisation rates per shot of 0.01, 1, 100 shot^{-1} . Maximal intensity corresponds to the coincidence or covariance signal of the $A + B$ (dominant) channel. False correlations are removed in the covariance maps.

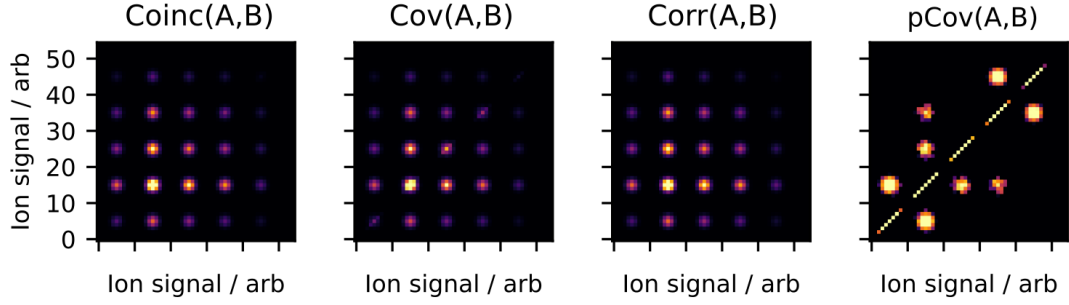


Figure 5.6: Simulated time-of-flight covariance maps for the reaction scheme in (5.5) at an ionisation rate, k_I , of 10 shot^{-1} and a linear power dependence such that $N_{\text{ion}} = Pk_I$. From left to right: Coincidence map, $\text{Coinc}(A, B)$; Total covariance map, $\text{Cov}(A, B)$; Correction term, $\text{Corr}(A, B)$; partial covariance map $\text{pCov}(A, B)$

where P is the constant of proportionality.

The total covariance map shows false correlations between ions that are not formed together. The partial covariance map accounts for the power dependence and reveals the correlations expected from the reaction scheme.

5.4.2 Recoil-Frame Angular Covariance

This section will outline how covariance between pixel events from a time-stamping camera such as PImMS can be calculated to determine correlations between ions. This has been demonstrated using PImMS data to determine angular correlations between ion pairs for isomer identification and delay-dependent photodynamics[58–60, 70, 121].

Individual ions can be distinguished after a mass calibration of a PImMS recorded ToF spectrum, and a ‘reference’ and ‘plotted’ ion are designated. Thereafter, covariance between each pixel in the ‘reference’ ion is calculated for each pixel in the ‘plotted’ ion. After this process, each pixel in the ‘reference’ ion image has an associated covariance map. In order to transform this into a single covariance map, each pixel covariance map is rotated such that all the pixels point along the same vector and are summed[70].

This process is illustrated in Figure 5.7 for the Coulomb explosion of a diatomic molecule that fragments into two ions, A and B . Panels (a), (b) and (c) show three

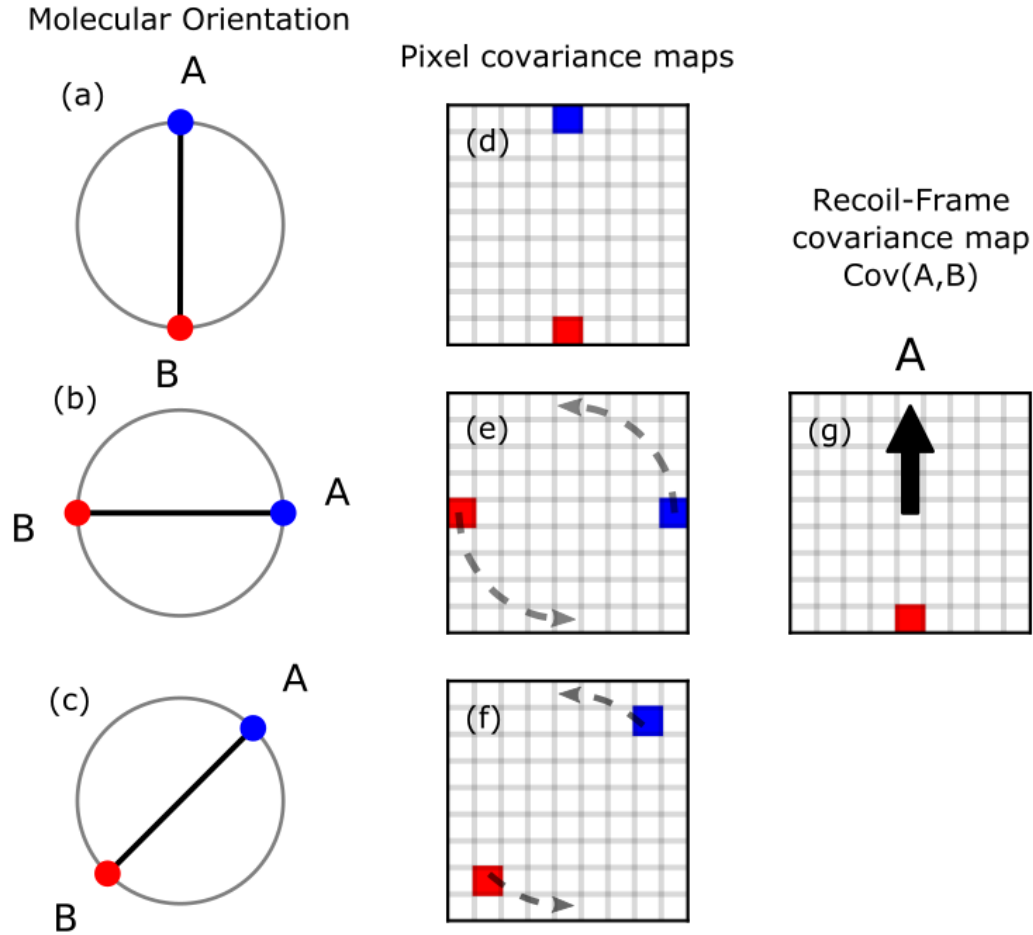


Figure 5.7: Demonstration of the procedure of recoil-frame angular covariance. The Coulomb explosion of the diatomic molecule AB produces the ions A and B which recoil in opposite directions. Panels (a), (b) and (c) show three possible orientations of the molecule at the moment of the Coulomb explosion. Panels (d), (e) and (f) show the correlations between three individual pixels (highlighted in blue) in the VMI image of A with all pixels of the VMI image of B (red). The pixels correspond to the initial molecular orientations in Panels (a), (b) and (c). Each pixel covariance map is rotated into a common recoil-frame (the relevant rotations are labelled with arrows in Panel E and F). The recoil-frame covariance map, $\text{Cov}(A,B)$, is shown in Panel (g) and shows the relative momentum of B is directed opposite to A , as expected. The arrow represents the velocity of A in the recoil-frame.

possible initial orientations of the molecule. Due to conservation of momentum, the ions recoil along the bond axis. The VMI images are recorded simultaneously using a pixel-based detector. Panels (d), (e) and (f) each show the covariance between an individual pixel (blue square) in the reference ion, A VMI image and all pixels of the plotted ion B VMI image. The pixel covariance maps correspond to the molecular orientations in Panels (a), (b) and (c). Each map is then rotated into a common recoil-frame such that the momentum vector of A lies along an arbitrary direction (vertical). The final recoil-frame covariance map is shown in Panel (g) and shows a back-to-back correlation. This map is denoted $\text{Cov}(A,B)$: the covariance of the momentum of B with respect to the momentum of A . Throughout this thesis, an arrow will point in the direction of the ‘reference’ ion momentum and the relative momentum of the ‘plotted’ ion will be displayed in the map.

5.4.3 Radial Covariance

This section will outline the technique of radial-mapping covariance technique. In this technique, the covariance between the radial distributions of two ion images is calculated (integrated over all angles of the image). This technique is similar to ToF covariance, in that covariance between two one-dimensional measures are used to create a two-dimensional map. As discussed in Section 5.4.1, in ToF covariance the variables X and Y are the time-of-flight signals, whereas in radial covariance X and Y represent the radial distributions of two ions in the image plane[229–231].

Figure 5.8 shows the simulated ion images for two ions, A and B ($N_{\text{shots}} = 1 \times 10^6$). A and B both have two velocity features, one uncorrelated channel and one correlated with the other ion. (A two-body break-up in this instance.) The right-hand plot shows the radial-radial covariance map for these ions. There is one region of correlation in the map corresponding to the radii of the two -body break up forming A and B . Radial-radial covariance can be a useful method of analysis when two or more covariance signatures are observed through recoil-frame angular covariance. Here, radial-radial covariance mapping can be used to filter

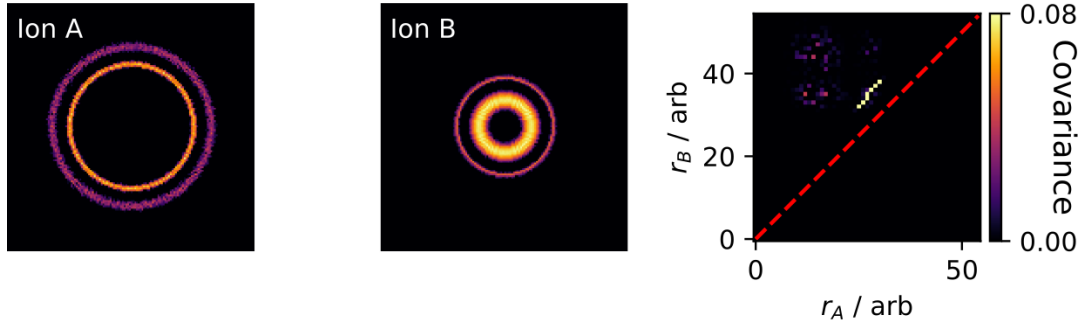


Figure 5.8: First two images show simulated images of ion A and B. Each image has two velocity features. Right: radial-radial covariance map between A and B. Covariance indicates the velocity at which both the two-body break-up occurs for each ion.

the covariance signatures according to the respective radii and help to assign the features in the recoil-frame covariance map.

5.5 Summary

This Chapter has discussed the principles of Coulomb explosion imaging and outlined its advantages as a technique for photodynamic investigations. The main methods of achieving a photoinduced Coulomb explosion and the underlying physics have also been discussed. The key differences between the form of the subsequent Coulomb explosion that each ionisation method initiates has also been discussed along with the subsequent relaxation processes that can occur.

Principles of covariance analysis as a statistical method to extract information from CEI experiments has also been discussed. Time-of-flight and recoil-frame angular covariance have been discussed in detail. Partial covariance has also been introduced to account for fluctuating parameters that directly affect the ion count. These methods of analysis are highly useful and are central to the work presented in the following chapters.

6

The Photochemistry of Thiophenone: 1

6.1 Introduction and Background

2(5H)-thiophenone, C_4H_4OS , (thiophenone herein) is a heterocyclic carbonyl compound, shown in Figure 6.1. Such heterocyclic compounds are considered fundamental building blocks in the synthesis of many organic compounds and show considerable interest in the field of molecular electronics as ultrafast switches[232]. Studying these singular units and better understanding the underlying electronic properties give an insight into larger molecules and allow for these to be studied in much greater detail.

Thiophene derivatives have been studied in the gas-phase extensively recently. Ashfold and coworkers studied the UV photochemistry of 2-bromothiophene across the wavelength range 265 – 245 nm in a multi-mass VMI set-up probed by a VUV ‘universal ionisation’ ($\lambda = 118.2$ nm) probe laser at a 25 ns delay [233]. They found that at all wavelengths, molecular products were formed arising from the atomic loss of a bromine. Complementary calculations suggest that internal conversion (IC) from a bound $\pi\pi^*$ excited state, *via* elongation of the C-S bond, offers a mechanism to an internally activated, ring-opened, ground state species. This state can subsequently undergo unimolecular decay to liberate a slow Br atom.

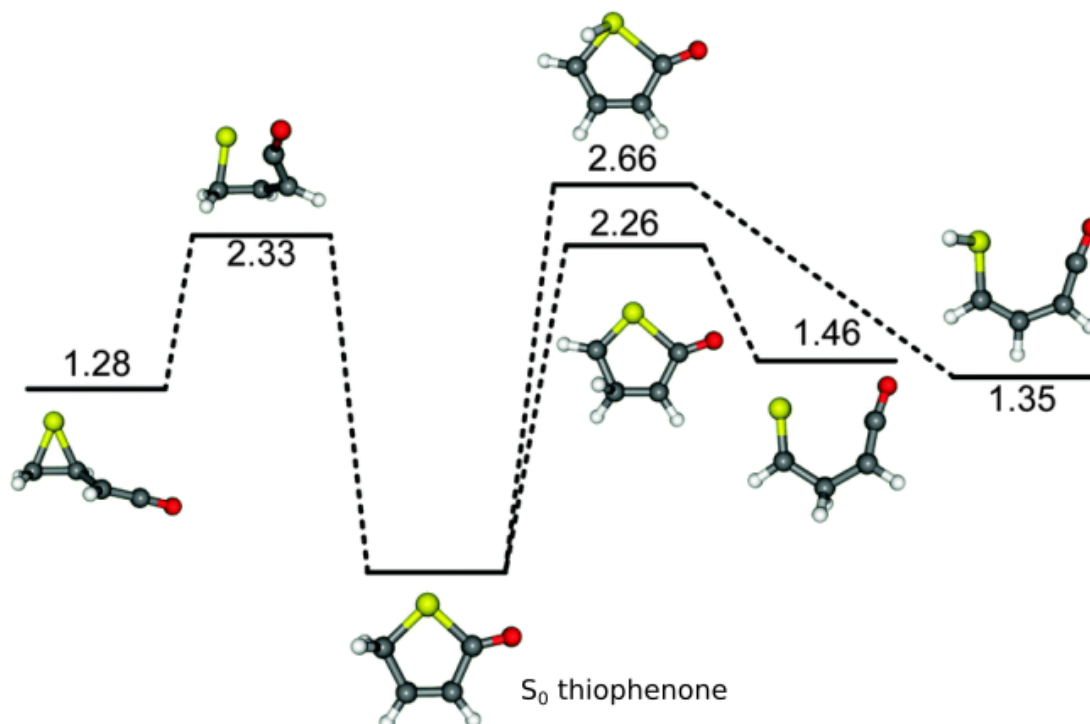


Figure 6.1: Ground state structure, S_0 of thiophenone and three possible ring-opened products calculated at the MP2/6-311+G(d,p) level of theory. All energies are in eV and are quoted relative to the equilibrium value of thiophenone. Figure adapted from Reference [234].

Murdock *et al.* showed that thiophenone undergoes ring-opening upon UV excitation at 267 nm in solution phase using UV-IR transient absorption spectroscopy to show that the parent, ring-closed, isomer was depleted upon UV excitation and signatures of the ring-opened isomers were observed[234]. This study lacked the temporal resolution to probe the ring-opening mechanism directly.

Rolles and coworkers employed time-resolved photoelectron spectroscopy (TR-PES) with a seeded extreme UV (XUV) FEL to trace the ultrafast ring-opening of gas-phase thiophenone molecules following UV photoexcitation[18]. Complementary *ab initio* electron structure calculations and molecular dynamic calculations of the excited and ground state molecules combine with the time-resolved photoelectron spectroscopy provided insights into the electronic and nuclear dynamics of gas-phase ring-opening reactions. TR-PES is a method that is sensitive to both electron and nuclear dynamics that govern most photoinduced reactions. Importantly,

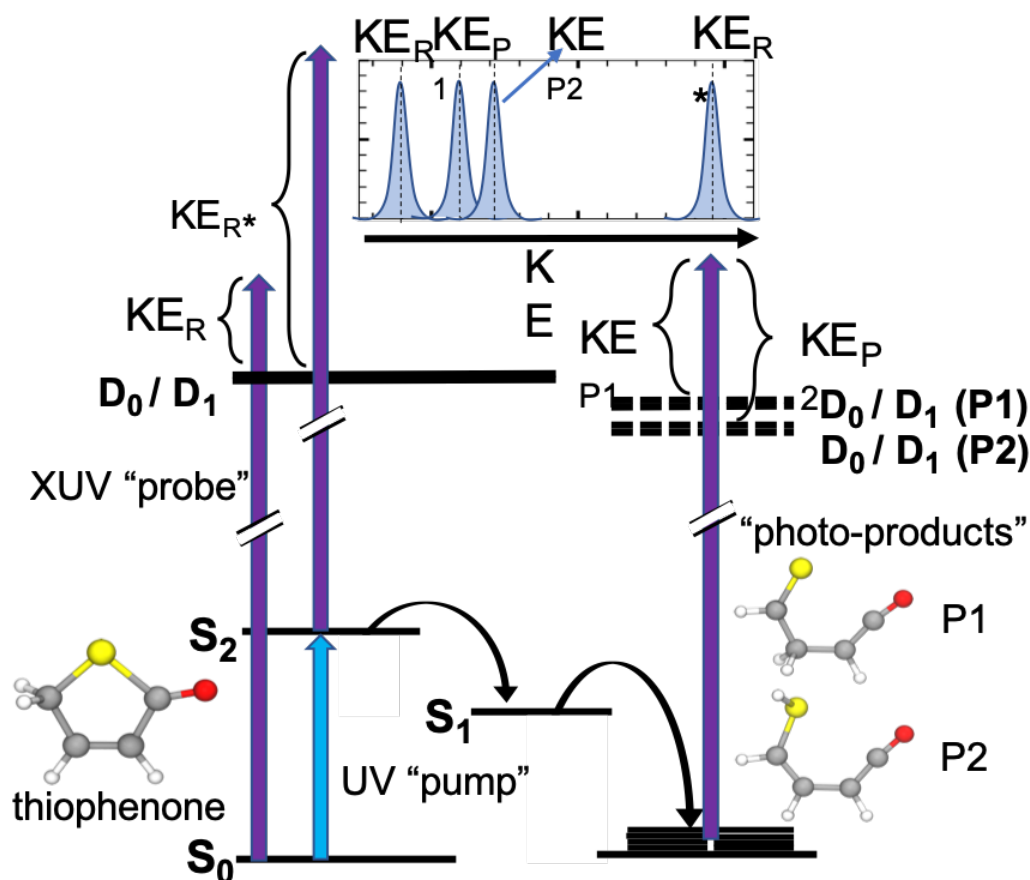


Figure 6.2: Ionisation scheme for the time-resolved photoelectron spectroscopy experiments performed by Rolles and coworkers[18]. Thiophenone molecules are excited by a UV pulse from the electronic ground state, S_0 to the electronically excited S_2 state. There, molecules evolve through the dark S_1 state to form ring-opened and ring-closed photoproducts such as those in Figure 6.1. XUV probe pulse is sufficiently energetic to ionise all products. Electron kinetic energy spectra were recorded at a number of pump-probe delays. See text for more details. Figure adapted from Reference [18].

the XUV probe pulses are sufficiently energetic to ionise all photoproducts in their electronic ground state (S_0), overcoming the long known problem of such experiments remaining insensitive to dynamics that evolve from an excited state back to a ground state remain undetected.

In the study, thiophenone was photoexcited from its ground S_0 state to an electronically excited (S_2) state by a UV pulse ($\lambda \approx 265$ nm). It evolves through an optically dark excited state (S_1) back to the ground electronic state of several ring-opened or ring-closed photoproducts, shown in Figure 6.1. The XUV pulse is sufficiently energetic to ionise thiophenone and all ground-state and excited-state

photoproducts into several ionic final states (D_0 , D_1 in Figure).

The most compelling signature of ring-opening was the short-lived electron signal appearing at a binding energy of ≈ 5 eV attributed to vertical ionisation of photoexcited molecules in the S_2 state to the D_0 and D_1 states. The increase in binding energy (to ≈ 9 eV) was evidence of the ultrafast decay from the S_2 state to the ground state (S_0) *via* S_1 . The complementary computational study found that ring-opening occurs *via* the stretching of the CS bond and ring-opening is complete within 350 fs. This scheme is illustrated in Figure 6.2.

The ring-opening of thiophenone was investigated in the gas phase at the Free-electron laser in Hamburg (FLASH) facility through Coulomb explosion imaging in combination with velocity map imaging and multi mass imaging. A series of experiments were conducted exciting the parent molecule with a UV photon at 267 nm. The single photon absorption at this wavelength is sufficient to cleave the carbonyl-sulfur bond and initiate ring-opening. The resultant product was then probed *via* strong-field infrared ionisation or inner-shell ionisation predominantly at the S(2p) atomic orbital[113].

In this Chapter, the dynamics and fragmentation of the UV excitation of thiophenone probed *via* strong-field infrared induced Coulomb explosion will be discussed.

6.2 Experimental Methods

The experimental apparatus used in this Chapter is described in great detail in Chapter 2 so a short description will only be provided here. Experiments were performed using the CFEL-ASG multipurpose (CAMP)[42, 93] chamber at DESY during a time-restricted beam-time.

6.2.1 Overview

A continuous stream of thiophenone seeded in either helium or xenon was introduced into the CAMP chamber[42] using a pulsed Even-Lavie valve[95] heated to 80°C. The beam passed through two skimmers before entering into the interaction region.

Here, the molecular beam was crossed by either one or two femtosecond laser pulses. The UV (≈ 120 fs) and IR (55 fs) pulses induced photo-isomerisation and a Coulomb explosion, respectively, in the target molecules. The beams are focussed onto a $40\text{ }\mu\text{m} \times 60\text{ }\mu\text{m}$ spot in the interaction region. The intensities of the coupled laser pulses could be adjusted as required experimentally with a waveplate in the fundamental arm of the laser. This change in intensity corresponds to pulse energies of 2 mJ ($I \approx 1 \times 10^{15} \text{ W cm}^{-2}$) to 0.65 mJ ($I \approx 1 \times 10^{14} \text{ W cm}^{-2}$) for the fundamental output, and $17\text{ }\mu\text{J}$ ($I \approx 1 \times 10^{12} \text{ W cm}^{-2}$) to $1.1\text{ }\mu\text{J}$ ($I \approx 4 \times 10^{11} \text{ W cm}^{-2}$) for the frequency tripled output. An automatic delay stage was used to vary the delay between the pump and probe pulses. The photoions and photoelectrons were velocity-mapped onto two position-sensitive detectors. The experimental set-up is shown in Figure 6.3.

6.3 Experimental Results: Pump and Probe Dynamics

This section will outline the experimental results of the UV- induced, IR- probe photo-excitation of thiophenone. The sole effects of the pump and probe pulses will first be explored before investigating the delay dependent signatures of the photochemistry triggered by the UV pulse in the pump-probe experiments.

By recording pump-probe experiments at a series of delays between laser pulses, information on any changes in fragmentation of thiophenone or changes in kinetic energy of the fragmentation can be observed. This will give insight into the UV excitation at this wavelength and may shed light on any isomerisation that may have occurred.

6.3.1 UV Pump Induced Dynamics

Firstly, the effect that the UV pump laser pulse alone has on thiophenone will be investigated. This is important to quantify as the role of this laser pulse is simply to initiate some photo-chemistry, specifically the ring-opening of thiophenone *via*

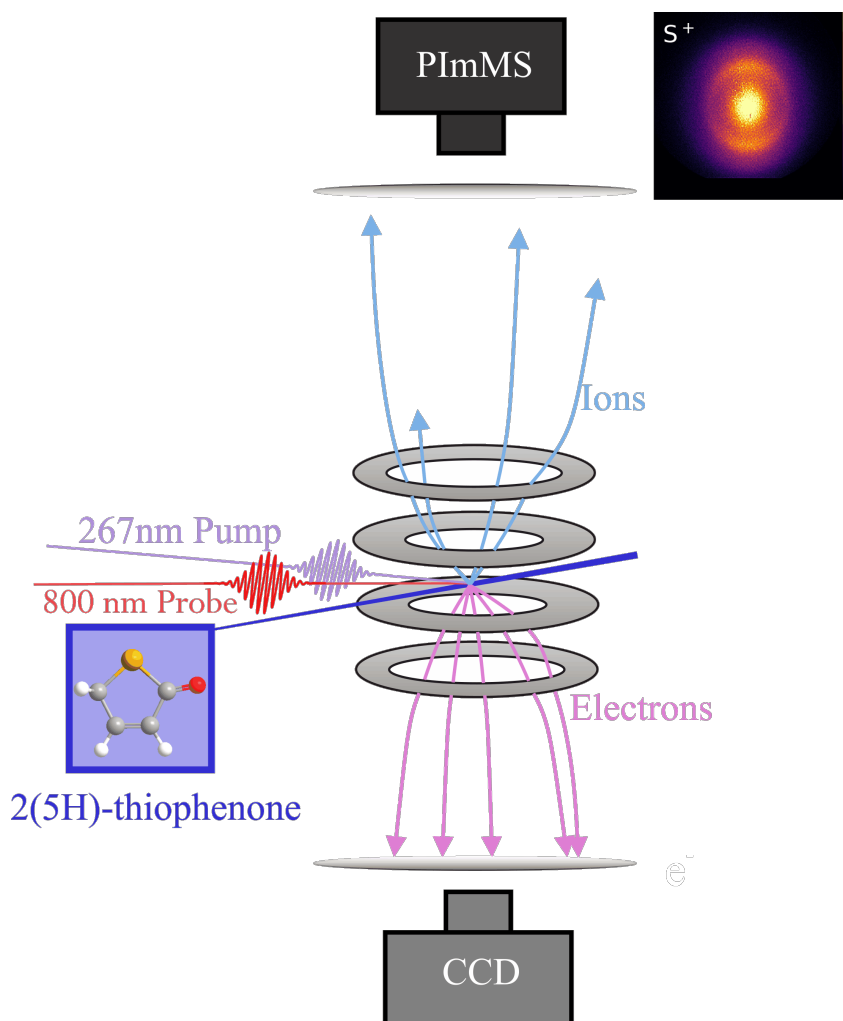


Figure 6.3: Experimental set-up at FLASH for the UV-IR pump-probe photo-excitation of thiophenone experiments.

the cleaving of a C-S bond. Therefore, ideally the UV pulse would produce no ions and simply isomerise a proportion of the target molecules.



Experimentally, this is difficult to achieve. In Time-of-Flight Mass Spectrometry (ToF-MS), only ions, and not neutral species, can be detected. The UV intensity could be reduced until no ions are detected in the Time-of-Flight (ToF) spectrum; however, in such a regime, it is impossible to know if the UV pulse has any effect. A compromise is to reduce the intensity of the UV pulse to a point where a small amount of ionisation and molecular fragmentation occurs (10s of ions per shot).

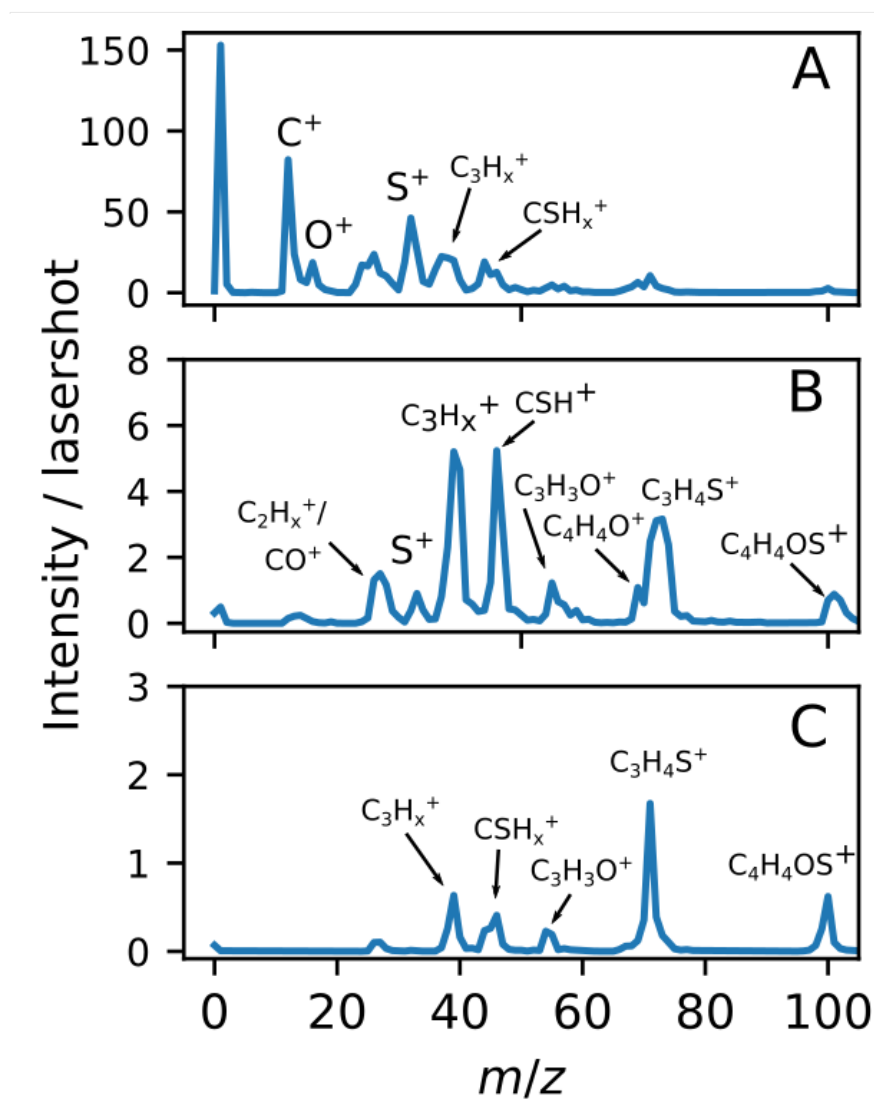


Figure 6.4: UV mass spectra recorded at varying laser intensities. Panels A, B, and C show the mass spectra recorded at maximal ($I \approx 4 \times 10^{12} \text{ W cm}^{-2}$), 30% ($I \approx 1 \times 10^{12} \text{ W cm}^{-2}$) and, 20% UV ($I \approx 3 \times 10^{11} \text{ W cm}^{-2}$) intensities, respectively. Key mass peaks are labelled in the mass spectra.

Further, the intensity should be such that the detection of atomic ions, such as S^+ and C^+ , is not observed as this would arise from multiple ionization and extensive fragmentation which is not the photochemical regime that we would like to study.

Figure 6.4 show the ToF spectra and associated mass spectra following the interaction of thiophenone with a UV pulse of varying laser intensities. Panel A of Figure 6.4 shows the spectrum obtained from the highest UV intensity ($I \approx 4 \times 10^{12} \text{ W cm}^{-2}$). It is clear that there is substantial fragmentation and ionisation

of the parent molecule. Most importantly, there are over 500 ions shot^{-1} recorded suggesting that there is widespread ionisation at this laser intensity. Further, a significant proportion of these are atomic carbon, oxygen, and sulfur ions which would require the absorption of many photons to dissociate and ionise. Lastly, the proportion of parent ion produced relative to the fragmented ions is very low. This suggests that very few parent molecules are intact after interaction with the UV pulse which in turn suggests that isomerisation is a very weak channel in such a regime.

Panel B of Figure 6.4 shows the spectrum obtained at 30 % UV intensity ($I \approx 1 \times 10^{12} \text{ W cm}^{-2}$). Much fewer ions are produced under these conditions ($\approx 50 \text{ ions shot}^{-1}$) which is more promising. A higher proportion of the parent, $\text{C}_4\text{H}_4\text{O}^+$, and high m/z fragments such as $\text{C}_3\text{H}_x\text{S}^+$ molecular fragments relative to the smaller fragments also suggests that there is much less multi-photon absorption. However, there is still significant fragmentation (C_2H_x^+ , C_3H_x^+ , CSH_x^+) and production of atomic ions ($1 \text{ S}^+ \text{ shot}^{-1}$, $0.5 \text{ C}^+ \text{ shot}^{-1}$). As the experiment can only detect ions, it is impossible to know how many neutral species are also present. It is therefore likely that many more dissociated neutral species are produced but remain undetected which would suggest that these are still undesirable laser intensities to investigate the isomerisation.

Panel C of Figure 6.4 shows the mass spectrum recorded at 20 % UV laser intensity ($I \approx 3 \times 10^{11} \text{ W cm}^{-2}$). At this laser intensity, fewer than 10 ions were produced per laser shot and no significant fragmentation was observed. This suggests that at this laser intensity there is very little multi-photon absorption producing ions and therefore more intact excited thiophenone.

At lower UV intensities, even fewer ions are produced but as mentioned previously, at the limit of zero ion production it is impossible to know if the UV photons are even initiating a ring-opening process. Further, the objective of the UV pulse is to interact with a significant number of target molecules to be able to probe the dynamics. Therefore, the UV intensity resulting in the mass spectrum in Panel C was deemed most suitable for pump-probe experiments. During a time-restricted

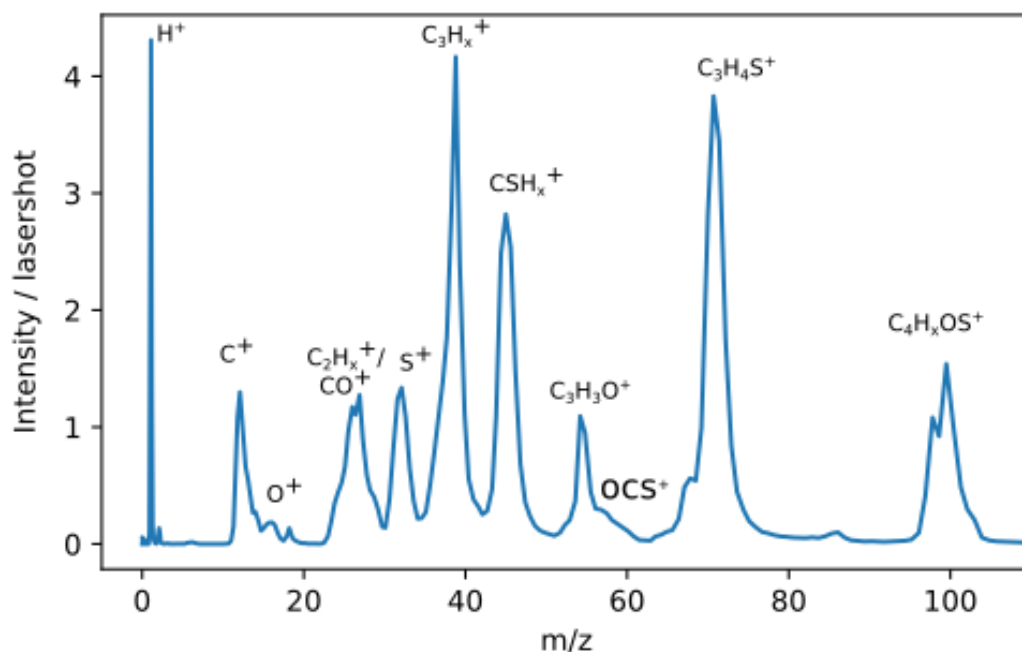


Figure 6.5: Mass spectrum obtained *via* strong-field ionisation of thiophenone by the IR pulse at the same optical laser transmission ($I \approx 5 \times 10^{14} \text{ W cm}^{-2}$) that produced the acceptable UV only conditions. See text for details.

beamtime, there has to be a compromise between the amount of pump-probe signal and the amount of unwanted multiphoton effects.

6.3.2 IR Probe Pulse Dynamics

The effect that the strong-field infrared pulse has on thiophenone must also be investigated to understand how the dynamics of the rapid photodissociation occur with no UV photon and the overall extent of Coulomb explosion that is induced. As the intensities of the UV (pump) and IR (probe) pulses are coupled, the transmission of the IR used in the probe only experiments must be the same as that which produced the UV only spectrum.

Time-of-Flight Analysis

The mass spectrum following the interaction of thiophenone with the probe only laser pulse is shown in Figure 6.5. Immediately, it is clear that there is significantly more fragmentation in comparison to the UV induced dynamics. This is expected as the strong-field removes multiple valence electrons which are present across the

molecule which will result in various fragmentation pathways. This is evidenced by the appearance of several atomic ions (H^+ , C^+ , O^+ , and S^+) per laser shot. There is also substantial fragmentation of the parent molecule into smaller molecular ions, such as C_2H_x^+ , C_3H_x^+ , and CSH_x^+ , which suggests multiple bonds breaking during the photodissociation. There are few multiply charged ions present in the mass spectrum, which suggests that the molecule typically undergoes further fragmentation rather than multiple ionising. The H^+ ion peak is very narrow which is likely a result of not detecting much of the high velocity ion.

An insight into the nature of the Coulomb explosion may be inferred by analysing the VMI ion images recorded by PImMS. These will reveal information on the kinetic energy release (KER) of ions resulting from the probe pulse and therefore indicate which channels are present and which ionisation regime is dominant.

Ion Image Analysis

The VMI ion images resulting from strong-field infrared ionisation of thiophenone are shown in Figure 6.6. The image for each ion in the mass spectrum is shown (except for the parent ion which has no velocity in the transverse plane and H^+ whose image does not fit on the detector) and the corresponding velocity distribution.

From the velocity distributions, a number of observations and pathways can be inferred. The peak at high radii in the C^+ and O^+ ion images suggest that these are formed from a multiply charged parent. This is to be expected as the more charge on the parent molecule, the more likely it is that there will be more fragmentation, and therefore more atomic ions present. These peaks are also very broad which is consistent with a multiple charged Coulomb explosion. Due to its molecular complexity, there are a large number of potential Coulomb explosion pathways, each with a different KER. This leads to the very broad velocity distribution that is observed.

The ionic fragments C_2H_x^+ , CO^+ , and S^+ all have a peak in velocity distribution at high radii. This suggests that these ions are predominantly formed from Coulomb explosion channels. As these ions are of greater mass than carbon and oxygen it

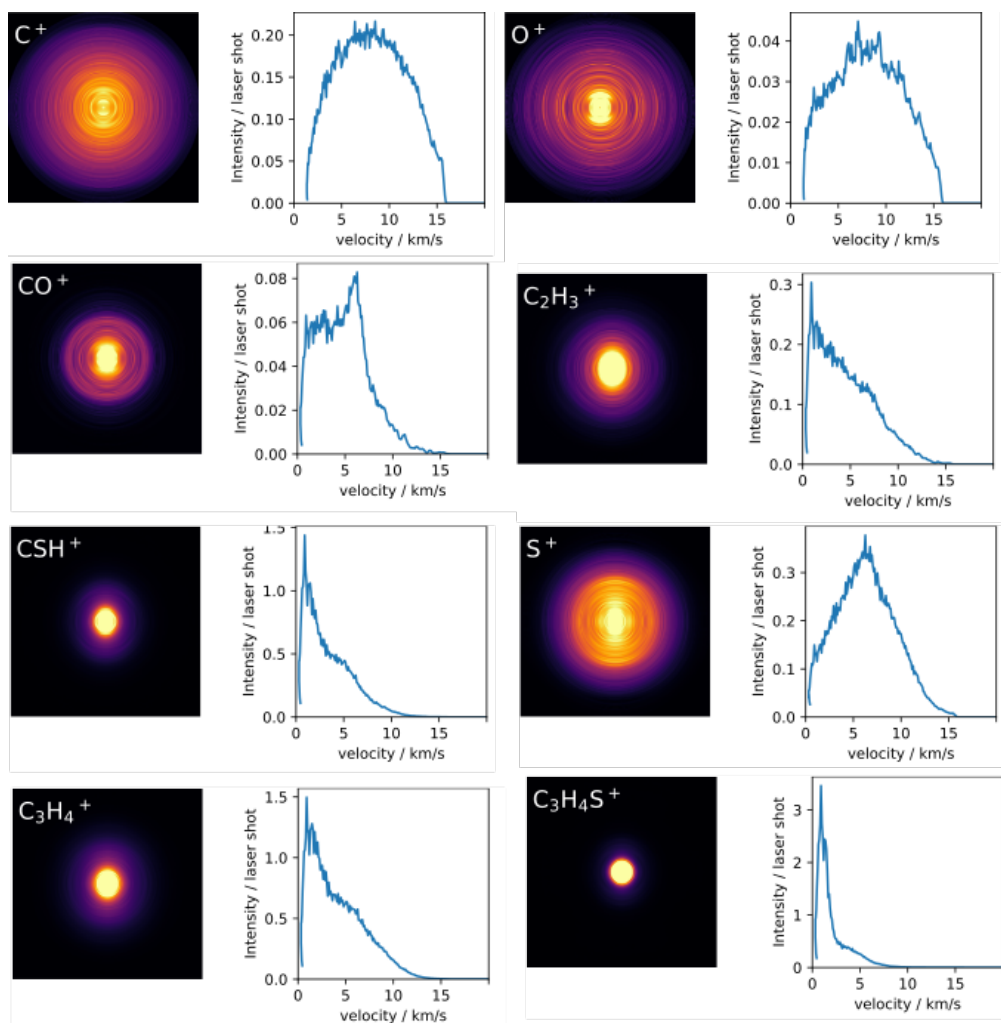
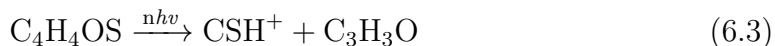
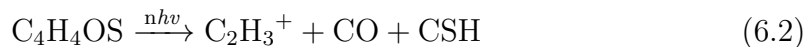


Figure 6.6: Abel inverted VMI images recorded by PImMS2 and corresponding velocity distributions of the ions observed in the probe only dissociation of thiophenone. See text for details and discussion.

would be expected that they would not carry as much kinetic energy as the lighter fragments. This is reflected in a lower peak in the respective velocity distributions. The CO^+ velocity distribution has a significant contribution at low radii.

The molecular fragments C_2H_3^+ , C_3H_x^+ , and CSH_x^+ also display a peak at high radii. This suggests that some of these fragments are produced from a Coulomb explosion channel. However, these ions have a more dominant feature at low radii. These ions are formed with very low kinetic energy and therefore are likely not formed from a Coulomb explosion channel. These ions are attributed to multiphoton or strong-field dissociative ionisation of the parent molecule, for example:



The heaviest molecular fragment, $\text{C}_3\text{H}_x\text{S}^+$, has a much lower velocity than the smaller fragments as it will always carry less energy than its cofragment(s) during break-up.

6.4 Experimental Results: Pump-Probe Excitation Dynamics

The section will discuss the pump-probe dynamics observed in these experiments. Two methods of detecting the ions were used during the experiments at FLASH. Firstly, as discussed the PImMS2 sensor records the x, y, t coordinates of ions arriving at the detector with a timing resolution of 25 ns. Secondly, an analogue-to-digital current (ADC) readout connected to the back of the MCP stack records the change in current across the MCP stack as ions hit the detector. This signal is converted to a digital signal and stored on the FLASH DAQ. The timing precision of the ADC readout is 500 ps which is in theory $50\times$ more sensitive than the PImMS camera. However, the ADC undergoes ‘ringing’ after a large ion peak and can take a short while (<10 ns) to stabilise. Even so, the improved timing resolution allows the disambiguation of ions that PImMS cannot resolve *i.e.* resolving individual methyl fragments, CH_x^+ . This cannot be used to give kinetic energy dependent ion yields but can give total ion yields for fragments that are otherwise unresolvable in the PImMS data.

The time delay between the UV and IR femtosecond pulses is controlled by an automatic delay stage. The UV pulse initiates the ring-opening and the IR pulse induces a Coulomb explosion in the parent molecule. By recording datasets at a series of delays before and after the temporal overlap of the laser pulses, the photo-induced dynamics and its evolution can be monitored.

6.4.1 Time-of-Flight Analysis

The overall effect that the combined UV and IR (UV-IR) laser pulses have on the ion yield are shown in the ToF spectrum in Panel A of Figure 6.7 in comparison to the pump- or probe- only data (at 20% laser transmission corresponding to laser intensities of $I_{\text{UV}} \approx 3 \times 10^{11} \text{ W cm}^{-2}$ and $I_{\text{IR}} \approx 5 \times 10^{14} \text{ W cm}^{-2}$). The green trace shows the ion intensity per laser shot, integrated over UV Early (UV pulse precedes IR pulse) pump-probe delays, and the blue and orange traces show the equivalent for pump- and probe- only data. The UV-IR ToF spectrum shows an increase in yield across all ions, except for the parent ion. Depletion of the parent is expected as more parent molecules are likely fragmented upon absorption of a UV photon.

The most notable enhancements in Panel A are the atomic species, H^+ , C^+ , O^+ , and S^+ . This is not unreasonable as the UV photon at least delivers a lot of energy to the system which will make fragmentation much more feasible. The KER of these ions that constitute the observed enhancements will help to understand the photoexcitation dynamics.

An enhancement in molecular fragment ions is also observed. This could be a result of greater Coulomb explosion after absorption of UV photon (and potential ring-opening), more dissociative ionisation or ionisation of neutral species produced after dissociation of the UV pulse. Again, the VMI ion images will shed more light on this.

Panel B shows the mass spectrum as recorded by PImMS (blue) and the ADC trace (red). Both broadly agree however the increased mass resolution as a result of the timing resolution of the ADC trace is apparent in the elucidation of peaks in the PImMS ToF profile and resulting identification of mass peaks. For instance, the peak assigned as C_3H_x^+ ($m/z \approx 39$) using PImMS in Figure 6.5 can be resolved completely into 5 distinct peaks with up to four protons attached to the propyl group. Other important examples include the identification of the peaks C_2^+ , C_2H_2^+ , C_2H_3^+ , and CH_xO^+ around $m/z \approx 27$ and the existence of otherwise unresolved de-protonated fragments at m/z of 72 and 45. Another interesting observation to note is the lack of parent ion observed in PImMS is contradicted by the ADC

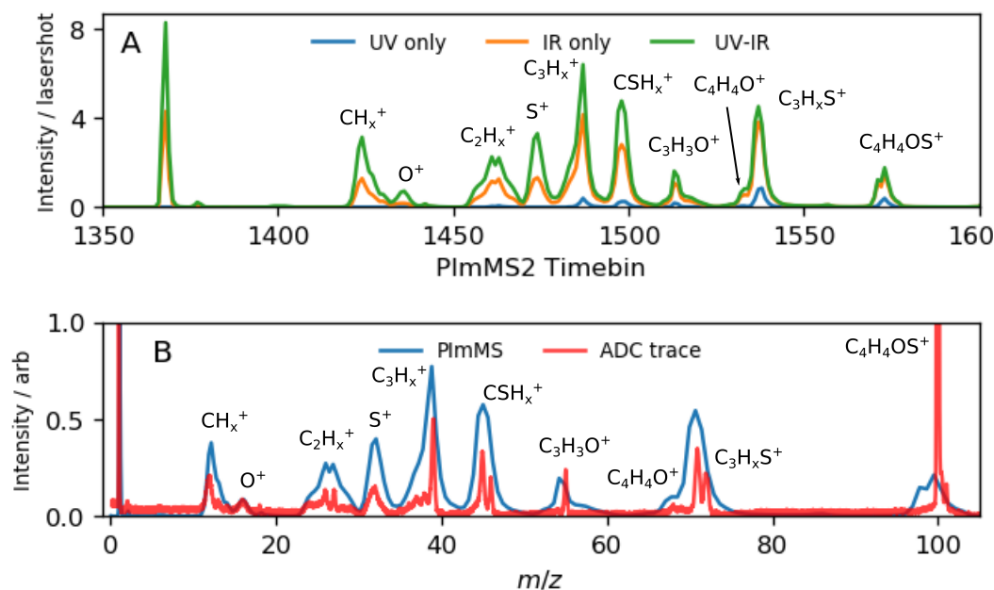


Figure 6.7: ToF spectra resulting from pump-probe interaction of thiophenone. Panel A shows the PImMS obtained ToF spectra under UV only, IR only, and UV-IR (integrated over all delays). Panel B shows the PImMS obtained UV-IR mass spectrum and the analogous spectrum acquired from the ADC trace. $I_{\text{UV}} \approx 3 \times 10^{11} \text{ W cm}^{-2}$ and $I_{\text{IR}} \approx 5 \times 10^{14} \text{ W cm}^{-2}$. See text for more details.

trace. The ADC trace is more representative as the pixels corresponding to the centre of the detector in PImMS are saturated by lighter ions with a low kinetic energy. Each pixel in the PImMS sensor array can only record up to four events per acquisition. This results in ‘dead’ pixels by the time in the acquisition that the parent arrives and therefore fewer of these ions can be detected. This issue is enhanced for the parent ion as it always has a low kinetic energy.

Although, the ADC trace cannot be used for velocity dependent ion yields it does provide a better resolved ToF spectrum that gives information into which ions and their relative intensities comprise unresolved peaks in the PImMS ion images. Total ion yields for these fragments can be determined which can be used in conjunction with the PImMS data to assign mechanisms and channels.

6.4.2 Velocity-dependent Channels

This section will discuss the observed pump-probe dynamics of velocity features in some VMI ion images. The observed channels fall broadly into one of two channels:

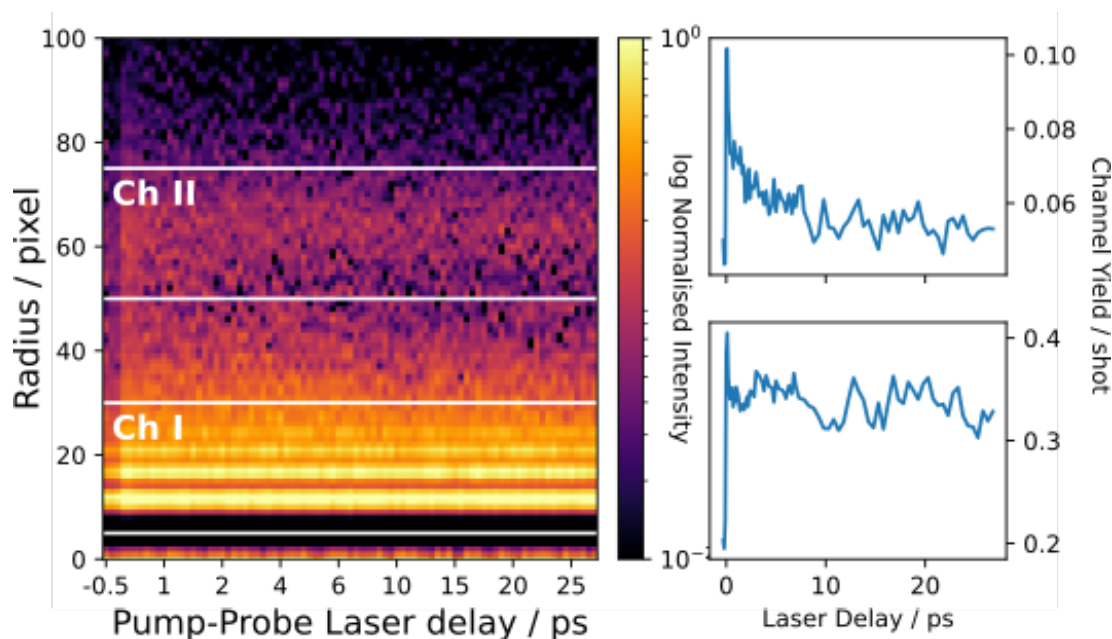


Figure 6.8: Left: Delay-dependent radial distribution of CSH_x^+ Abel inverted ion images. Channels are labelled and the corresponding radial ranges. Top right: delay-dependent Channel II yield of CSH_x^+ ions. Bottom right: delay-dependent Channel I yield of CSH_x^+ ions. Images recorded with laser intensities of $I_{\text{UV}} \approx 3 \times 10^{11} \text{ W cm}^{-2}$ and $I_{\text{IR}} \approx 5 \times 10^{14} \text{ W cm}^{-2}$.

Channel I and Channel II. Channel I corresponds to an ion yield enhancement in ions with a very small or zero kinetic energy. Channel II corresponds to a similar enhancement in ions with a greater kinetic energy release. These channels are illustrated in Figure 6.8 for the CSH_x^+ ion, as an example.

Figure 6.8 shows the delay-dependent radial distribution, obtained from inverted CSH_x^+ ion images, as a function of pump-probe delay. The radial distribution intensities are plotted on a logarithmic scale to illustrate the two channels simultaneously. Channel I is marked approximately between 5 and 30 pixels and Channel II between 50 and 75 pixels. The UV late (probe only) is shown as negative pump-probe delays (left) and both channels show a rapid enhancement around 0 ps; after which there is a sustained enhancement in the respective channels. Channel II is a much weaker channel, approximately $10\times$ less intense than Channel I. This trend is reflected across all ions that exhibit these channels.

Channel I

This section will explore Channel I in more detail — the enhancement in yield of some low kinetic energy ions. This Channel is observed in molecular ions: C_2H_x^+ , C_3H_x^+ , CSH_x^+ , $\text{C}_3\text{H}_x\text{S}^+$. The VMI ion images from the experiments performed at different pump-probe delays show that low kinetic energy molecular fragment ions of these ions are enhanced at UV early pump-probe delays *i.e.* when the UV pulse precedes the IR pulse. The enhancement in these ions is prompt following temporal overlap of the laser pulses.

In general, once the enhancement has occurred, the yield of the low kinetic energy channel remains constant with further increasing pump-probe delay. Low kinetic energy ions suggest that they are borne as the sole charge in its surroundings and therefore not part of a Coulomb explosion.

Figure 6.9 show the delay-dependent yields of Channel I ions and the corresponding kinetic fit. The yields are fitted using a least-squares fitting algorithm according to the following equation consisting of a Gaussian function, $G(t)$, a cumulative distribution function, $\text{CDF}(t)$, and the convolution of an exponential decay, $E(t)$:

$$f(t) = G(t) + \text{CDF}(t) + E(t) + y_0 \quad (6.5)$$

where $G(t)$ is a Gaussian defined:

$$G(t) = A_G \exp\left(\frac{-(t - t_0)^2}{2\sigma^2}\right) \quad (6.6)$$

$\text{CDF}(t)$ is the cumulative distribution function:

$$\text{CDF}(t) = \frac{A_{\text{CDF}}}{2} \left\{ 1 + \text{erf}\left(\frac{t - t_0}{\sqrt{2}\sigma}\right) \right\} \quad (6.7)$$

where t is the pump-probe delay, t_0 is the pump-probe delay where the two laser pulses are overlapped temporally, σ is the standard deviation of the Gaussian distributions, and A_i are the relative weightings. The exponential decay is given by:

$$E(t) = \text{Heaviside}(t - t_0) A_{\text{exp}} \exp\left(-\frac{t - t_0}{\tau}\right) \quad (6.8)$$

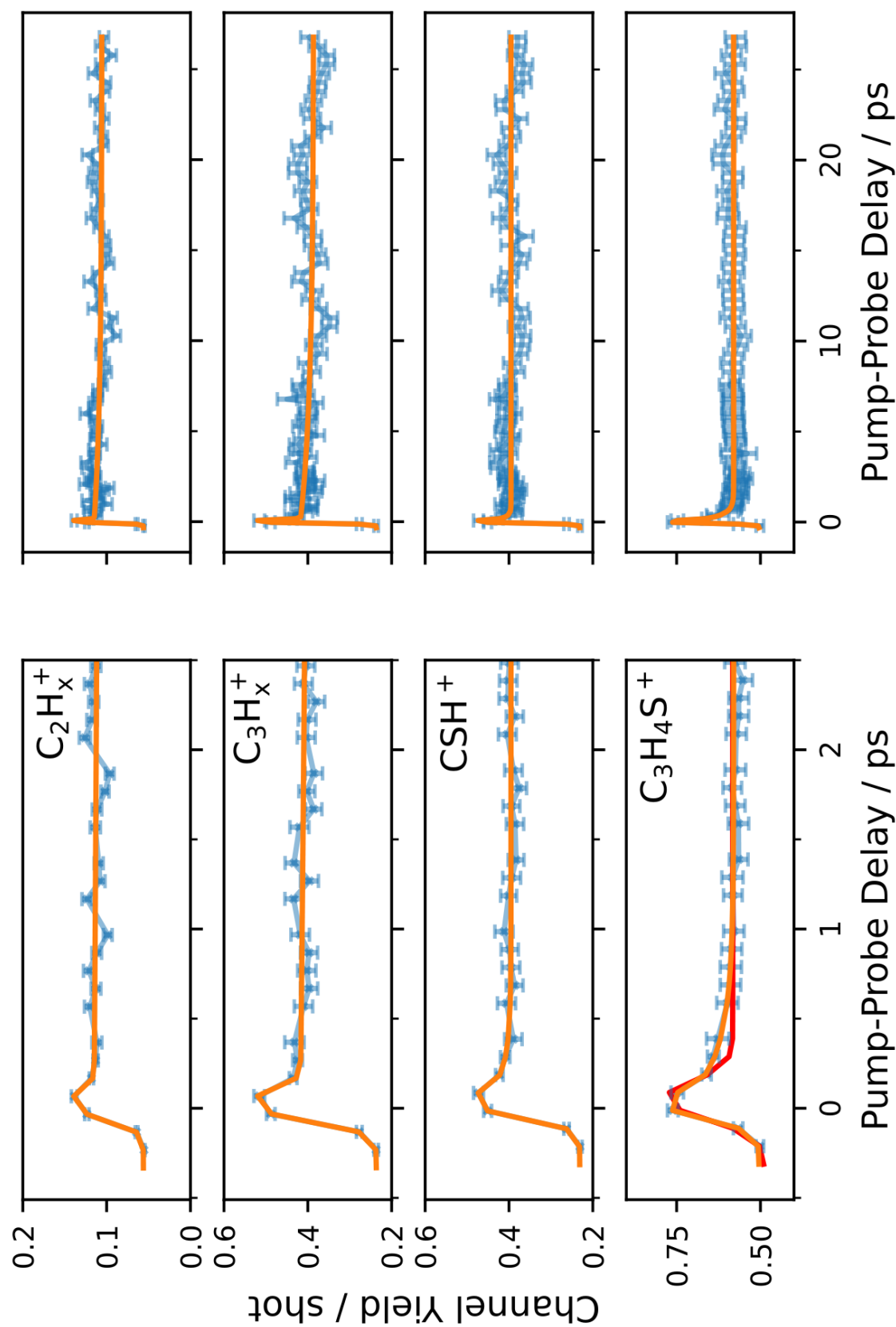


Figure 6.9: Delay dependent ion yields in Channel I in $C_2H_x^+$, $C_3H_x^+$, CSH^+ , $C_3H_4S^+$. Channels were determined by restricting the radial ranges of Abel inverted images to the enhanced peak. The left-hand plot shows the short-time delay dependence ($t_0 - 0.5$ ps - $t_0 + 2.5$ ps). The right-hand plot shows the full delay-dependence (up to $t_0 + 30$ ps). The blue trace (and associated error) shows the shot normalised Channel I yield of the ion, the orange trace shows the dynamical fit (Equation (6.5)) to the experimental data. The red trace (bottom left) shows the dynamical fit excluding the exponential decay. Images recorded with laser intensities of $I_{UV} \approx 3 \times 10^{11} \text{ W cm}^{-2}$ and $I_{IR} \approx 5 \times 10^{14} \text{ W cm}^{-2}$. See text for more details.

where τ is a decay constant. This exponential decay is subsequently convoluted with a Gaussian with the same parameters as $G(t)$.

The Gaussian function accounts for the cross-correlation of the two laser pulses. Ionisation is enhanced when the the laser pulses are overlapped temporally resulting in a rapid increase and subsequent decrease in ion yield (over all radii). The cumulative distribution function accounts for the overall enhancement in the Channel yield following the cross-correlation. The exponential decay accounts for the time taken for the ions to attain the eventual yield. This exponential decay function is convoluted with a Gaussian function to avoid an unreasonably sharp decay which is not resolvable in these experiments.

Figure 6.9 shows the delay-dependent ion yields of Channel I for the relevant ions (C_2H_x^+ , C_3H_x^+ , CSH_x^+ , $\text{C}_3\text{H}_x\text{S}^+$ from top row). The left column shows the short-time delay-dependence ($\approx t_0 + 2$ ps) and the right column shows the long-time delay-dependence. The experimentally observed channel yield (blue crosses) and the dynamic fit (orange line) are in excellent agreement for each ion. The ion yield undergoes a rapid enhancement around t_0 as the laser pulses overlap temporally and subsequently quickly converges (< 0.5 ps) at a constant yield. The long-time (up to $\approx t_0 + 25$ ps) channel yields (right column) show that the yields do not change at longer delays.

The fitted parameters for the Channel I ion yields are shown in Table 6.1. The fitted values for the pump-probe delay corresponding to t_0 are in good agreement at ~ 30.80 ps. (In the plotted ion yields, this arbitrary value has been subtracted from the experimental delays such that t_0 corresponds to 0 ps.) The values for the standard deviation of the Gaussian function is 65 ± 2 fs. This corresponds to a full width at half maximum (FWHM) of ~ 155 fs which is a comparable with previous experiments performed at FLASH[58, 59]. The time constants of the exponential decay functions for the ions have values less than 0.25 ps, representing a very fast dynamical process.

The fitted parameters, A_G , A_{CDF} , A_{exp} describe the relative contributions of the Gaussian, cumulative distributive, and convoluted exponential decay functions,

Ion	t_0 / ps	σ / fs	τ / ps	A_G	A_{CDF}	A_E
$C_2H_x^+$	30.81 ± 0.01	65 ± 9	0.11 ± 0.01	0.48	0.29	1
$C_3H_x^+$	30.81 ± 0.01	70 ± 4	0.05 ± 0.02	0.16	0.59	1
CSH^+	30.79 ± 0.01	62 ± 6	0.2 ± 0.1	0.79	1	0.61
$C_3H_xS^+$	30.79 ± 0.01	70 ± 4	0.12 ± 0.01	0.49	0.13	1.0

Table 6.1: Table summarising the fitted parameters of the Channel I yields. See text for more details and discussion.

respectively. The exponential decay function typically has the largest contribution though the Gaussian functions contribute appreciably.

The effect of the exponential terms is demonstrated for the $C_3H_xS^+$ ion (bottom row), which shows a fit excluding the convoluted exponential decay term (red line). This fit clearly does not describe the early pump-probe dynamics adequately. This behaviour is reflected in the other ions and justifies the necessity of the exponential function.

Channel II

The second delay dependent channel observed in this dataset, Channel II, is an enhancement in the high kinetic energy channel of a number of different molecular fragment ions and atomic ions at UV early delays. This channel is similar to Channel I except that it involves higher kinetic energy ions that are borne as a result of a Coulomb explosion. This channel is much weaker than Channel I.

The enhancement is prompt akin to Channel I but has a longer decay constant. Channel II is present in the following ions: O^+ , CH_xO^+ , S^+ , $C_2H_x^+$, $C_3H_x^+$, CSH_x^+ , $C_3H_xS^+$. Channel II was illustrated in Figure 6.8 for the CSH_x^+ ions. As can be seen from the corresponding delay-dependent channel yield, the enhancement in Channel II ions is sustained for approximately 10 ps before returning to UV late (IR only) comparable yields. This trend is broadly followed across all ions that show this channel with the exception of the CH_xO^+ and $C_3H_xS^+$ ions, which will be discussed separately.

Figure 6.10 shows the delay-dependent channel yields of some of Channel II ions and the corresponding kinetic fit. The yields were fit according to Equation

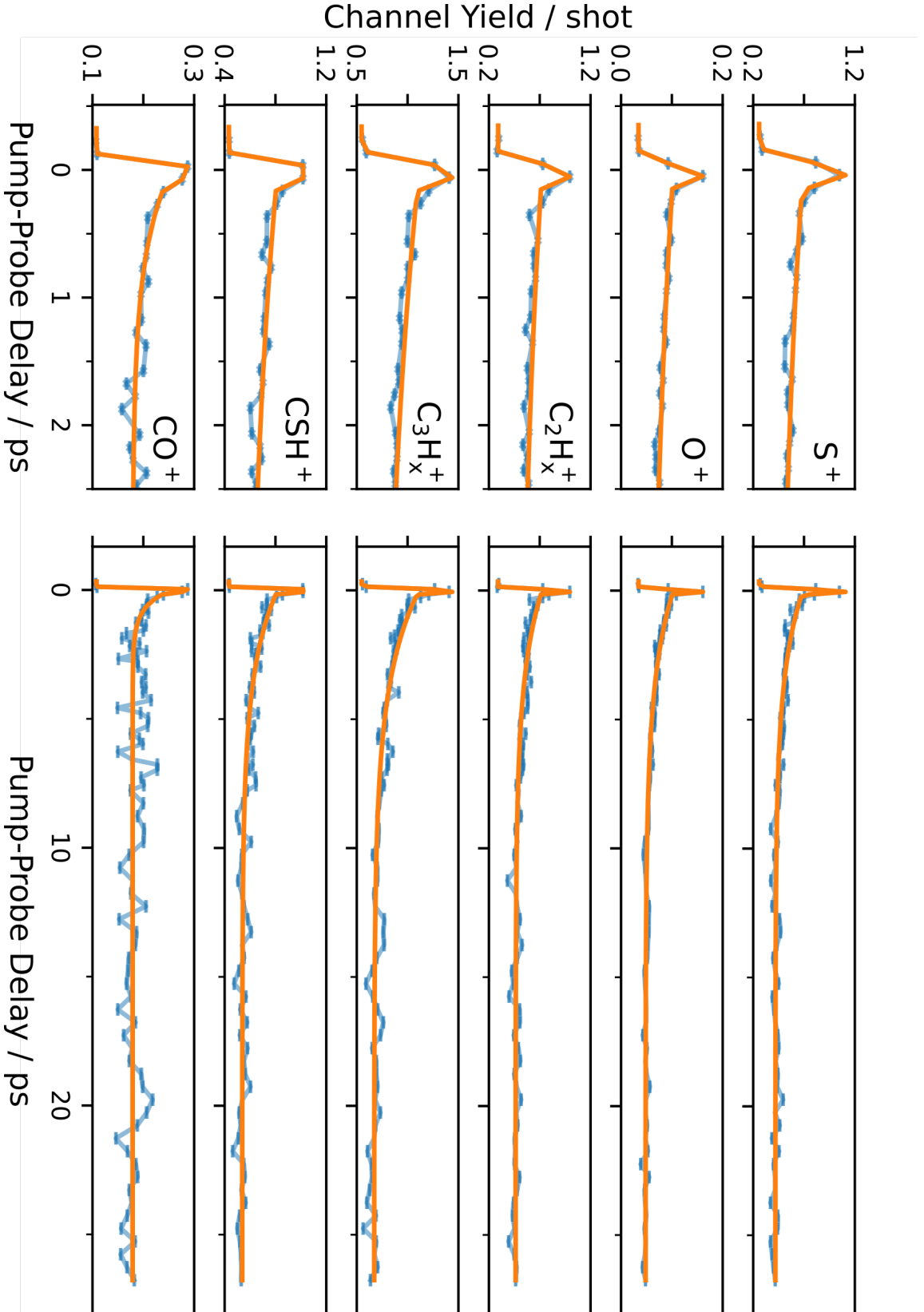


Figure 6.10: Delay-dependent ion yields in Channel II. Channels were determined by restricting the radial ranges of Abel inverted images to the enhanced peak. The left-hand plot shows the short-time delay dependence ($t_0 - 0.5$ ps - $t_0 + 2.5$ ps). The right-hand plot shows the full delay-dependence (up to $t_0 + 30$ ps). The blue trace (and associated error) shows the shot normalised Channel I yield of the ion, the orange trace shows the dynamical fit (Equation (6.5)) to the experimental data. Images recorded with laser intensities of $I_{UV} \approx 3 \times 10^{11}$ W cm $^{-2}$ and $I_{IR} \approx 5 \times 10^{14}$ W cm $^{-2}$. See text for more details.

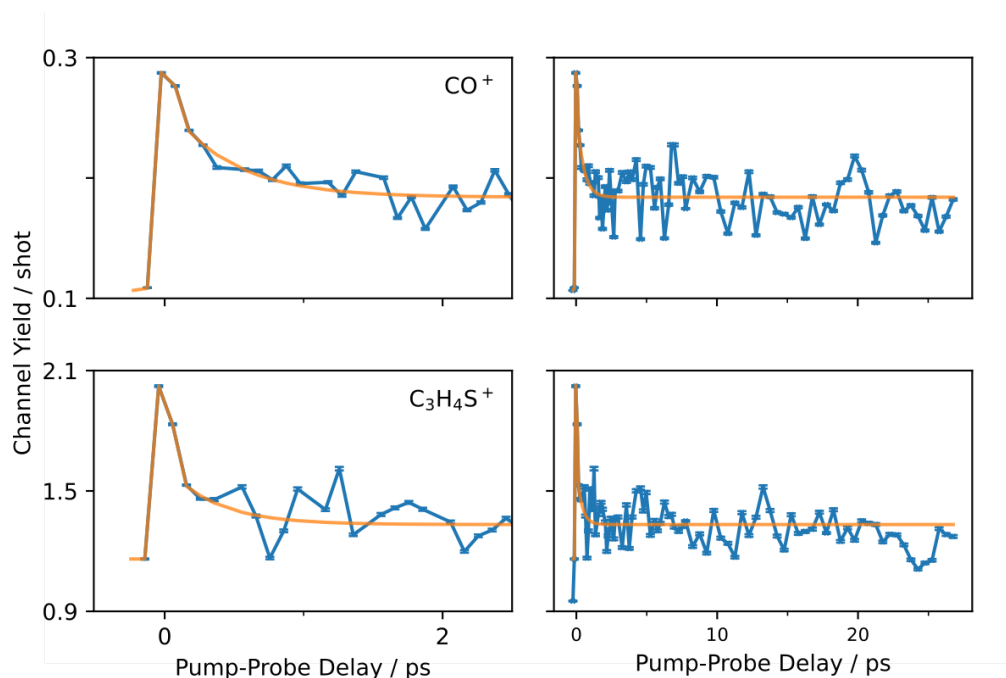


Figure 6.11: Delay-dependent ion yields in Channel II of CO^+ and $\text{C}_3\text{H}_4\text{S}^+$. Channels were determined by restricting the radial ranges of Abel inverted images to the enhanced peak. Experimental observed ion yields for each delay is shown in blue and fits are shown in red line according to Equation (6.5). Images recorded with laser intensities of $I_{\text{UV}} \approx 3 \times 10^{11} \text{ W cm}^{-2}$ and $I_{\text{IR}} \approx 5 \times 10^{14} \text{ W cm}^{-2}$. See text for more details

(6.5) and the associated parameters are summarised in Table 6.2. As with Figure 6.9, the left column shows the short-time delay-dependence ($\approx t_0 + 2 \text{ ps}$) and the right column shows the delay-dependence over the entire delay range measured. The experimentally observed channel yield (blue crosses) and the dynamic fit of Equation (6.5) (orange line) are in good agreement. Each channel displays the cross-correlation expected as a result of the temporal overlap of the two laser pulses. As alluded to previously, the channel yields for the S^+ , C_2H_x^+ , C_3H_x^+ , CSH_x^+ ions are qualitatively similar where the initial enhancement around t_0 eventually decays to a yield comparable to IR only.

Figure 6.11 shows the corresponding channel yield and kinetic fits for the CH_xO^+ and the $\text{C}_3\text{H}_x\text{S}^+$ ion. Again, the short-term delay-dependence is shown in the left-column and the long-time delay-dependence in the right-column. The behaviour of the channel in these ions is different from the previously discussed ions in that the ion yield does not significantly decay after the initial enhancement. This behaviour

Ion	t_0 / ps	σ / fs	τ / ps	A_G	A_{CDF}	A_{exp}
S^+	30.84 ± 0.01	68 ± 4	3.1 ± 0.4	1.0	0.25	0.42
O^+	30.83 ± 0.02	30 ± 113	3.4 ± 0.2	1.0	0.06	0.23
C_2H_x^+	30.83 ± 0.06	31 ± 92	3.2 ± 0.4	1.0	0.14	0.21
C_3H_x^+	30.82 ± 0.01	61 ± 5	3.4 ± 0.4	1.0	0.18	0.64
CSH_x^+	30.82 ± 0.01	43 ± 5	3.0 ± 0.4	1.0	0.15	0.40
CH_xO^+	30.80 ± 0.01	40 ± 20	0.45 ± 0.21	1.0	0.41	0.45
$\text{C}_3\text{H}_x\text{S}^+$	30.80 ± 0.01	67 ± 10	0.35 ± 0.22	1.0	0.4	0.2

Table 6.2: Table summarising the fitted parameters of the Channel II yields. See text for more details and discussion.

is more similar to that of the Channel I ions where the enhancement was prompt and sustained over long pump-probe laser delays. This suggests that for the CH_xO^+ and $\text{C}_3\text{H}_x\text{S}^+$ ions formed in their respective Channel II kinetic energy range are formed regardless of pump-probe delay after absorption of a UV photon.

The pump-probe delay corresponding to t_0 for this channel agrees well for all ions at ~ 30.8 ps. This value is within 50 fs agreement to the t_0 measured in Channel I which corresponds to a single pump-probe delay stage. The standard deviations are also in relative agreement ranging from 30 – 68 fs and within the error range. These values are also in reasonable agreement with the value of 65 fs measured for Channel I. The decay constant for the exponential decay of the Channel in all ions, except for the $\text{C}_3\text{H}_x\text{S}^+$ and CH_xO^+ ions, is ~ 3 ps and suggests that these ions are borne from the same excited state of thiophenone. The corresponding parameter for the CH_xO^+ and $\text{C}_3\text{H}_x\text{S}^+$ ions are 0.45 ps and 0.35 ps, respectively. These represent a much faster decay as discussed above and are more comparable to the decay constants observed in Channel I ions.

6.4.3 Discussion

Figure 6.12 summarises the Channels observed following the UV-IR photo-excitation of thiophenone that have been discussed in this section. The Figure also outlines a possible mechanism that explains the dynamics observed at this laser intensity.

The blue and red boxes show the products arising from Channel I and Channel II, respectively. The probe only pulse produces ions in both Channels which are

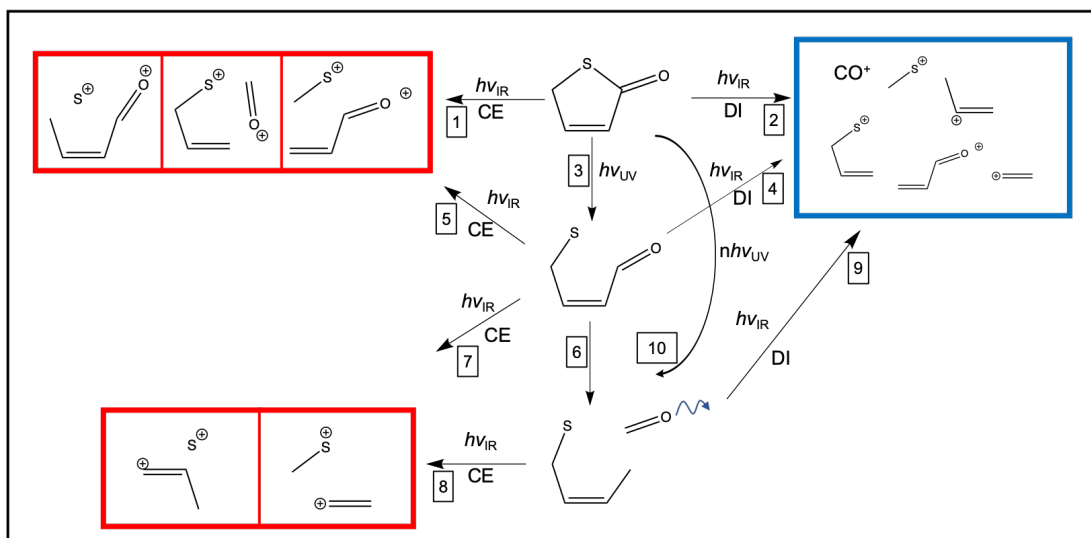


Figure 6.12: UV/IR photoexcitation scheme devised to explain the existence of Channels and ions observed in the present work. See text for more details.

both enhanced upon the absorption of a UV photon. These channels are shown by the two horizontal arrows marked 1 and 2 in Figure 6.12. In Channel I, the IR pulse dissociatively ionises thiophenone resulting in the formation of a single low kinetic energy molecular fragment ion *e.g.* CSH_x^+ . Alternatively, the IR pulse can multiply ionise thiophenone resulting in a Coulomb explosion and the formation of two or more charged fragments with a greater KER.

Arrow 3 marks the absorption of a UV photon. Here, thiophenone is assumed to be ring-opened but could be in an excited ring-closed state or the ground (ring-closed) state of thiophenone. On the arrival of the IR pulse, the excited parent can undergo a number of channels, arising in either the production of Channel I or Channel II ions. Firstly, the IR pulse can dissociatively ionise the product to form a variety of singly charged ions (arrow 4) and one or more neutral cofragments. The ring-opened photoproducts have markedly lower IPs[18, 235] and are therefore more likely to be dissociatively ionised which would explain the observed enhancement in Channel I ions. Arrow 10 represents the multiphoton UV absorption, resulting in dissociation of thiophenone molecules. Dissociated fragments could be ionised and contribute to Channel I.

Secondly, the IR pulse can induce a Coulomb explosion in the ring-opened

product (or excited ring-closed thiophenone). This would account for Channel II where high KER ion yields enhancements were observed for S^+ , CSH_x^+ , $C_2H_x^+$, $C_3H_x^+$, and O^+ ions (arrows 5 and 7). These Coulomb explosion pathways will be supported through covariance analysis in the following Section.

The observation of a different behaviour in the Channel II yields in the CH_xO^+ and $C_3H_xS^+$ ions is of note. After the initial enhancement, there is no discernible decrease in yield with increasing pump-probe delay. This suggests that once the UV photon is absorbed, regardless of when the IR pulse arrives the yield of these ions does not change. This would indicate that the molecule from which these derive is fundamentally different to that before the UV pulse and is potentially a signature that ring-opening has occurred. The KER does not change as a function of pump-probe delay which suggests that there is no dissociation or fragmentation of the molecule.

This photoexcitation scheme will be revisited after the following section which will investigate ion correlations derived from Channel II using covariance analysis.

6.5 Ion correlations through Covariance Analysis

Angular covariance was calculated for a series of possible ion pairs that displayed a Channel II to ascertain any correlations between ions. Recoil-frame angular covariance was introduced in Chapter 5. Covariance was calculated for a dataset integrated over all UV early pump-probe delays to improve the statistics. Figure 6.13 shows the angular covariance maps of the ion pairs that exhibited significant angular covariance. The white arrow represents the direction of momentum of the reference ion (labelled) and the covariance of the second ion is plotted.

The observed covariances fall in two categories: back-to-back (BTB) and non-back-to-back covariance. BTB covariance occurs where the angular recoil of the plotted ion is directed 180° to the reference ion, *i.e.* the ions recoil in exactly opposite directions.

Non-back-to-back angular covariance occurs when the recoil of fragments is not 180° to each other. In general, this is the case in a multi-body break up, where a

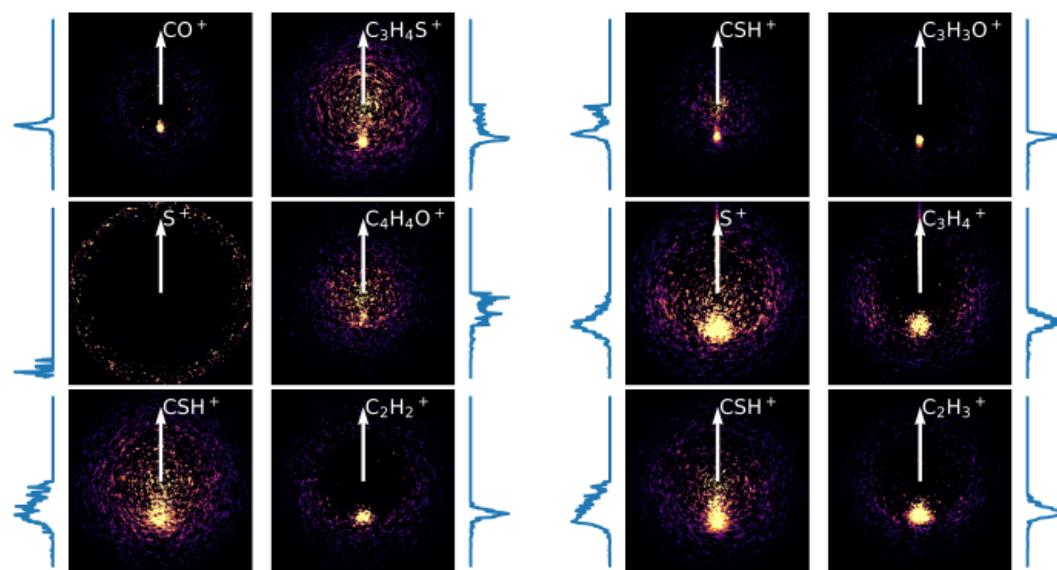


Figure 6.13: Angular Covariance of ion pairs integrated over all laser shots. By row, and left to right: CH_xO^+ and $\text{C}_3\text{H}_x\text{S}^+$, CSH_x^+ and $\text{C}_3\text{H}_x\text{O}^+$, S^+ and $\text{C}_4\text{H}_4\text{O}^+$, S^+ and C_3H_x^+ , CSH^+ and C_2H_2^+ , and CSH_x^+ and C_2H_3^+ . The white arrow represents the direction of the reference ion, which is labelled. The radial projection of each angular covariance map is shown along the edge. See text for more details.

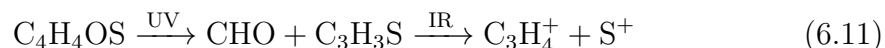
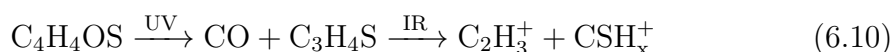
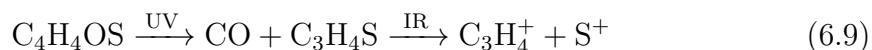
third (or more) fragment carries some momentum of the Coulomb explosion, which effects the trajectories and momenta of the plotted and reference ions.

BTB angular covariance is observed in this data between CH_xO^+ and $\text{C}_3\text{H}_x\text{S}^+$, CSH_x^+ and $\text{C}_3\text{H}_x\text{O}^+$, S^+ and $\text{C}_4\text{H}_4\text{O}^+$ ions. For these Coulomb explosion pathways, two charges are initially on the parent molecule which subsequently dissociates promptly and the remaining fragments accelerate according to Coulomb's Law, as outlined above. BTB covariances are characterised by a very sharp single feature owing to the rigid initial restrictions of such a break up *i.e.* momentum conserving between two fragments resulting in a back-to-back recoil and very limited positions of initial charge location resulting in a well-defined KER. The BTB covariance is most clearly observed in the CH_xO^+ and $\text{C}_3\text{H}_x\text{S}^+$ and CSH_x^+ and $\text{C}_3\text{H}_x\text{O}^+$ ions. The BTB covariance can be seen in the radial projections, where other than the noise toward the centre, sharp and very well-resolved peaks are observed.

The BTB signature is only just visible in the S^+ and $\text{C}_4\text{H}_4\text{O}^+$ channel and not when the sulfur is the reference ion. This suggests that this fragmentation

pathway is a very minor channel. This was indicated from the ToF spectrum which shows the $C_4H_4O^+$ is a minor ion. Although S^+ is an abundant ion in the photodynamics, this is not the only pathway that can result in its formation as will be seen later. However, the fact that this channel appears much weaker than the other BTB channels does reveal something of the photodynamics regardless. It suggests that the other BTB channels ($CH_xO^+/C_3H_xS^+$ and $CSH_x^+/C_3H_xO^+$) are more strongly preferred pathways than this one. The $C_4H_4O^+$ could be typically further fragmented resulting in a many-body break-up. Another possibility is the prompt elimination of the CO moiety from the parent results in the C_4H_4O fragment rarely appearing at all. The elimination of CO was identified by Pathak *et al.*[18] as a pathway after ring-opening and within 2 ps. Such an elimination would leave the C_3H_4S fragment. Alternatively, the Coulomb explosion of thiophenone could produce a neutral CO and two other charged species.

The non-back-to-back covariance observed in the other ions could derive from such a Coulomb explosion process, as all the remaining fragments could be formed from this pathway:



Contrary to the BTB covariance, these covariance display broad peaks. This is expected for a multi-body break up where at least one other fragment must carry some momentum from the system. This will cause some blurring to the relative velocities observed. Further, the location of charges and inter-charge separations have more variance which leads to a range of Coulomb explosions and final velocities. The radial integral of respective covariance maps is shown in Figure 6.14. The BTB covariances display sharper peaks than the other covariances as explained above. In these plots, the covariance is plotted as a function of angle relative to the reference ion over the radial range where the covariance is observed. Each

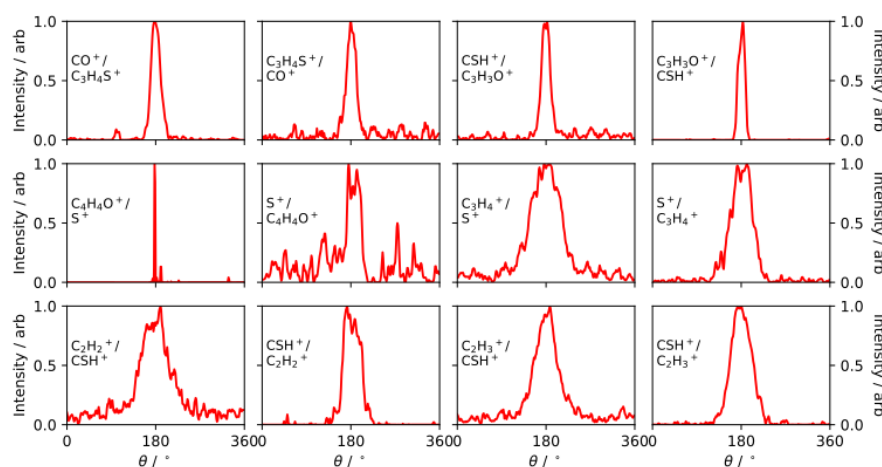


Figure 6.14: Radial integration of the covariance maps shown in Figure 6.13 over the radii of the feature of interest. Ion pairs are labelled on respective plot, where the first ion denotes the reference ion, and the second ion denotes the radial integral of the plotted ion. By row, and left to right: CH_xO^+ and $\text{C}_3\text{H}_x\text{S}^+$, CSH_x^+ and $\text{C}_3\text{H}_x\text{O}^+$, S^+ and $\text{C}_4\text{H}_4\text{O}^+$, S^+ and C_3H_x^+ , CSH_x^+ and C_2H_2^+ , and CSH^+ and C_2H_3^+ . See text for more details

plot displays a strong covariance signal at around 180° . The $\text{CH}_x\text{O}^+/\text{C}_3\text{H}_x\text{S}^+$ and $\text{CSH}_x^+/\text{C}_3\text{H}_x\text{O}^+$ show the most narrow distributions. These are BTB covariances and are expected to be very sharp with a distinct radius and necessarily an opposite recoil. The third BTB covariance ion pair, $\text{S}^+/\text{C}_4\text{H}_4\text{O}^+$, is as mentioned above a very weak channel. In the covariance maps and radial projection, it is even unclear if there is a BTB covariance signal above the noise, but in the $\text{S}^+/\text{C}_4\text{H}_4\text{O}^+$ plot (second column, second row), there is a clear covariance signal at 180° . No covariance was observed in the reversed ion pair.

The radial integral of the non back-to-back covariances are shown in the rest of the plot. These peaks are notably much broader for the reasons discussed above.

The radial peaks in the covariance maps can be seen in the ion images which suggests that these are real correlations and that they are interrelated to Channel II. Although, this analysis has shown that certain ion pairs arising from Channel II are correlated; a UV delay-dependent enhancement has not yet been observed. The next section will explore this.

6.5.1 Delay-dependent Covariance

Figure 6.15 shows the UV Late (left column) and UV Early (middle column) recoil-frame angular covariance maps calculated for the ion pairs discussed. The third column shows the covariance map obtained from UV early data where the number of laser shots is chosen such that the number of reference ions considered is equal to those in the UV Late data set (left column). This allows for a fairer comparison of the two data sets. Each covariance map in the same row (*i.e.* the same ion pair) is plotted on the same intensity scale to observe absolute changes in the covariant signal. Covariance maps are defined as $\text{Cov}(\text{Reference}, \text{Plotted})$. The white arrow represents the direction of the reference ion and the relative momentum of the plotted ion is shown.

The covariance maps, $\text{Cov}(\text{CH}_x\text{O}^+, \text{C}_3\text{H}_x\text{S}^+)$, are shown in the first row. There is an overall slight increase in the covariance signature for this ion pair. This ion pair does show the strongest signature at UV Late delays, which indicates that this is a major two-body pathway for thiophenone under these conditions.

The delay-dependent covariance maps, $\text{Cov}(\text{CSH}_x^+, \text{C}_3\text{H}_x\text{O}^+)$, are shown in the second row. There is an enhancement in the absolute covariance of the feature of interest at UV early delays. This indicates that this channel contributes to the observed ion yields of Channel II for these ions. There is an appreciable covariance signal at UV late delays; again suggesting that this represents a significant channel in the IR only dynamics. However, the pathway is enhanced after UV photoexcitation.

The covariance maps, $\text{Cov}(\text{C}_4\text{H}_4\text{O}^+, \text{S}^+)$, are shown in the third row. As discussed previously, this is a relatively weak channel. The signature is resolved in the full UV Early data set; however, in the other two data sets it is harder to comment categorically whether the ion correlation is observed at all. The data sets require more statistics to make a concrete assessment on whether a delay-dependence exists for this ion pair. The covariance maps, $\text{Cov}(\text{S}^+, \text{C}_3\text{H}_x^+)$, are shown in the next row. For this ion pair, there is a clear enhancement in the covariance signature at UV early delays. At UV Late delays, there is no evidence of any covariance. The UV Early covariance map in the third column has more noise than the corresponding

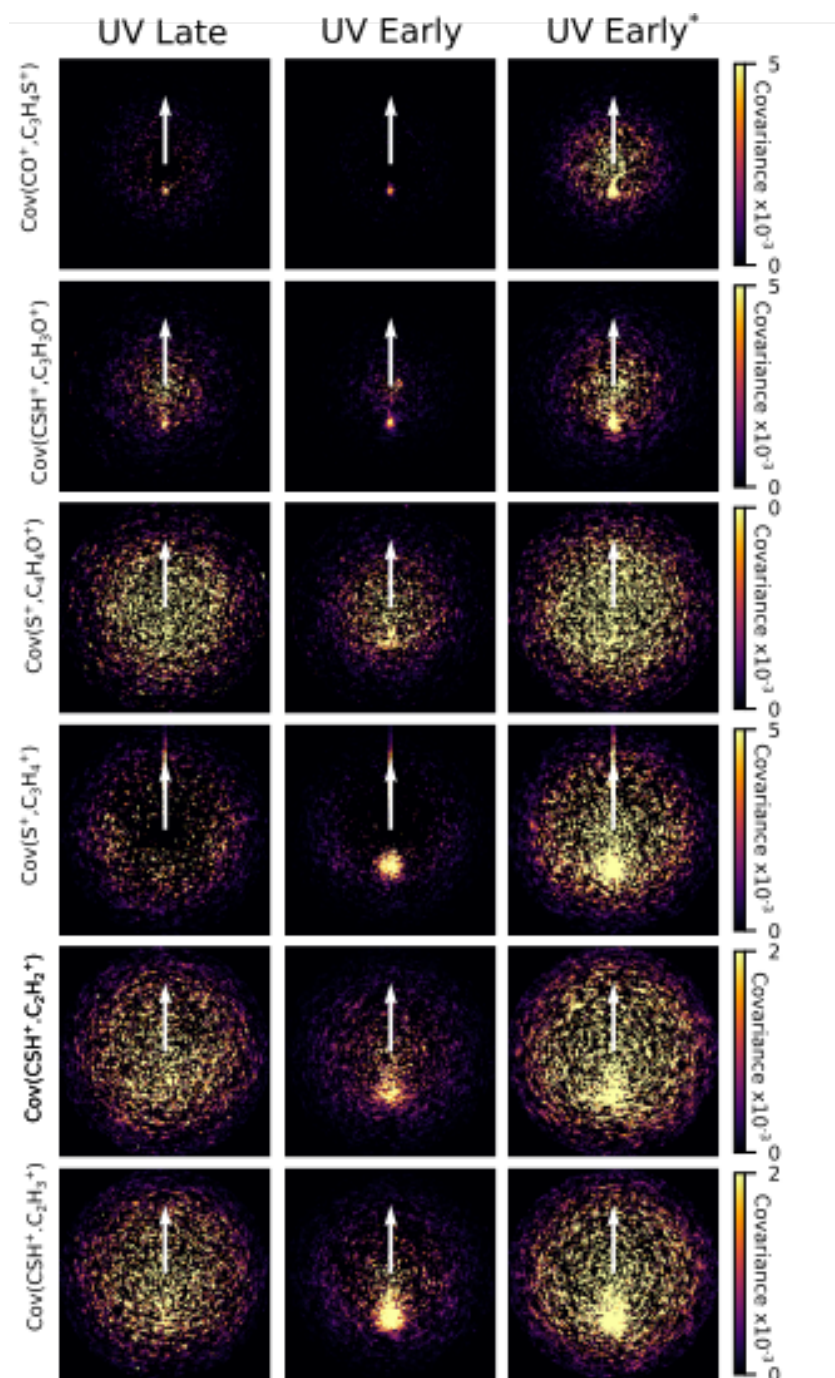


Figure 6.15: UV early and late comparative covariance maps. The absolute covariance maps are labelled UV late, UV Early, and UV Early*, where the asterisk denotes that the same number of reference ions were used as in the UV Late dataset to create a more comparative covariance map. Each row shows a different ion pair. From the top row (first ion denotes the reference ion): $\text{cov}(\text{CH}_x\text{O}^+/\text{C}_3\text{H}_x\text{S}^+)$; $\text{cov}(\text{CSH}_x^+/\text{C}_3\text{H}_x\text{O}^+)$; $\text{cov}(\text{S}^+/\text{C}_4\text{H}_4\text{O}^+)$; $\text{cov}(\text{S}^+/\text{C}_3\text{H}_x^+)$; $\text{cov}(\text{CSH}_x^+/\text{C}_2\text{H}_2^+)$; and $\text{cov}(\text{CSH}_x^+/\text{C}_2\text{H}_3^+)$. Arrow denotes the direction of recoil of the reference ion.

full data set; however the same covariant feature is clearly observed. This indicates that this ion correlation is dependent on the absorption of the UV photon. From this information, it is difficult to infer anything further about the underlying UV photodynamics.

The covariance maps, $\text{Cov}(\text{CSH}_x^+, \text{C}_2\text{H}_2^+)$ and $\text{Cov}(\text{CSH}_x^+, \text{C}_2\text{H}_3^+)$, are shown in the final two rows, respectively. Both these covariance maps show similar dynamics to the $\text{S}^+/\text{C}_3\text{H}_x^+$ ion pair to wit a UV dependent covariance signal that is not observed in the UV Late data set. Again, this indicates that these Coulomb explosion pathways arise from some UV photochemistry. This could be a consequence of the ring-opening process or an increased Coulomb explosion of ring-closed thiophenone after absorption of the UV photon.

The delay-dependent covariance signatures observed in $\text{Cov}(\text{S}^+, \text{C}_3\text{H}_x^+)$, $\text{Cov}(\text{CSH}_x^+, \text{C}_2\text{H}_2^+)$, and $\text{Cov}(\text{CSH}_x^+, \text{C}_2\text{H}_3^+)$ all involve ions that sum to form $\text{C}_3\text{H}_x\text{S}$ *i.e.* thiophenone without a CH_xO fragment. This strongly suggests that these ion correlations derive from the Coulomb explosion of a $\text{C}_3\text{H}_4\text{S}$ fragment. This implies that the CO moiety is eliminated after the absorption of a UV photon before the remaining fragment undergoes Coulomb explosion. It is unclear whether the elimination of CO occurs after the UV photon is absorbed or as part of the Coulomb explosion process. The recoil covariance signatures are directed at 180° from the reference ions with a slight angular distribution. Simulations could be performed to ascertain whether these covariances are consistent with a CO elimination and subsequent Coulomb explosion or a simultaneous break-up.

Figure 6.16 again shows the UV late and early angular covariance maps between the CH_xO^+ and $\text{C}_3\text{H}_x\text{S}^+$ ion pair, magnified around the covariance signature. The third plot shows a UV early covariance map calculated from the same number of shots as constituted the UV late dataset in order to make a fairer comparison. Both datasets show a strong covariance signal at a large radius. This corresponds to the Coulomb explosion of the intact parent into the two respective fragments. The increase in intensity at UV early delays is a result of an increased likelihood of Coulomb explosion after UV photon absorption. The broad nature of the peak

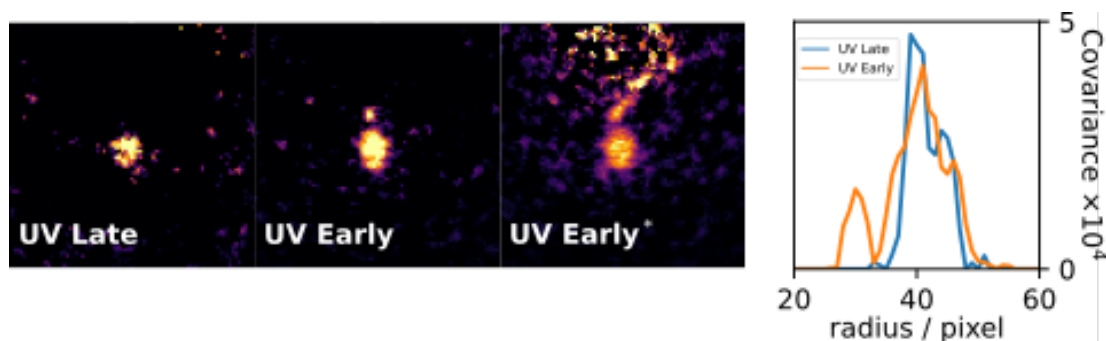


Figure 6.16: Comparative recoil-frame angular covariance maps of CH_xO^+ and $\text{C}_3\text{H}_x\text{S}^+$. First three covariance maps are zoomed plots of the corresponding ion pairs covariance maps shown in Figure 6.15. The final plot shows the normalised radial projections of the UV early and UV late angular covariance maps.

is likely a result of varying charge locations and proportion of energy that is required to break the residual bonds and different excited states of thiophenone accessed, see Figure 6.2.

The UV early datasets show the appearance of a new covariance signature at lower radii in comparison to the UV late data. The signature is also visible in the truncated dataset which shows that this cannot be a statistical issue leading to the covariance not converging in the UV late dataset. This suggests that at UV early delays, a novel Coulomb explosion channel occurs that could be a result of a new structure, *i.e.* a ring-opened isomer. Previous work in the literature show that the ring-opened isomers of thiophenone, see Figure 6.1, [18, 234, 235] are more extended and the sulfur and carbonyl moieties are much further separated. A Coulomb explosion from these isomers would result in a weaker repulsion and hence a smaller KER, as is observed. Alternatively, ring-closed thiophenone could be excited to different potential energy surfaces, as in Figure 6.2 and observed by Rolles and coworkers[18], and lead to different fragmentations pathways and correspondingly different velocities.

This covariance signal does not change with increasing delay as has been observed in previous experiments on other systems[59]. Allum *et al.* showed that a UV photon dissociated CH_2ICl to form neutral CH_2Cl and I fragments. These fragments are subsequently ionised at varying pump-probe delays and the covariance signal moved to lower radii with increasing delay as the fragments are further separated.

Therefore, the covariance was used to track the extent of the dissociation. Whereas in the current work, the covariance tracks the isomerisation of an intact molecule. The fact that the BTB covariance signal does not reduce and is a distinct signal when integrated over all UV early pump-probe delays shows that the signal is not a result of ionisation of dissociated neutral fragments.

Probing the covariance signature at finer pump-probe laser delays in the present work is not viable. Realistically, the dataset could only be separated into three sub-categories of pump-probe laser delays: 0.1 ps, +3 ps, and 3 ps – 30 ps. Unfortunately, the statistics in each sub-delay were not sufficient for the angular covariances to converge and reveal information on the ring-opening dynamics.

The normalised radial projection of each covariance map is shown in the right-hand plot of Figure 6.16 for comparison. The invariant covariance signature, attributed to the Coulomb explosion of the intact molecule reassuringly lie at the same radius and the UV-dependent feature can be clearly seen.

6.5.2 Discussion

This section will elaborate on the discussion of Channels I and II with reference to the photoexcitation scheme in Figure 6.12 using the ion correlation information gleaned from covariance analysis.

There is evidence that the ion covariance between a number of ion pairs is enhanced at UV early delays. This suggests that these Coulomb explosions are the cause of the Channel II enhancements. The UV-dependent covariance enhancement was particularly strong for the S^+ and $C_3H_x^+$ and CSH_x^+ and $C_2H_x^+$ ion pairs. These both indicate the elimination of a CO fragment (arrow 6) from an excited thiophenone molecule and a subsequent Coulomb explosion of the C_3H_xS fragment (arrow 8). The Channel II decay constants associated with these ions are each ≈ 3 ps. This decay constant could be associated with elimination of the CO fragment from the excited ring-opened molecules as identified by Pathak *et al.*[18] to occur within 2 ps.

The S^+ , $C_3H_x^+$, $C_2H_x^+$ could also be produced directly from the ring-opened isomer *via* a concerted CO eliminated Coulomb explosion (arrow 7). Although, strong covariance between these ions has been observed and discussed it is difficult to be sure of the structure of the molecule at the point of Coulomb explosion. The broad radial and angular distribution of the recoil-frame angular covariance calculated in these ions imply that a number of pathways are possible and to unpick these fully extensive simulations and more high statistic experiments should be performed. Simulations of the expected covariances arising from concerted and sequential CO eliminations and subsequent Coulomb explosions could resolve these ambiguities[236].

Additionally, upon CO elimination, the resultant product could be dissociatively ionised to again produce a singly charged ion and one or more neutral cofragments (arrow 9). Finally, arrow 10 shows the multi-photon UV absorption of thiophenone to neutrally dissociate the parent into a number of different products which could also then be dissociatively ionised.

An additional UV-early covariance signature in the CH_xO^+ and $C_3H_xS^+$ ion pair, at a lower velocity than the UV-late covariance signature was observed. This suggests that upon absorption of a UV photon a novel Coulomb explosion pathway that forms these ions in covariance is created. This could be a result of a weaker Coulomb explosion due to a more extended ring-opened isomer. Alternatively, a number of excited states of thiophenone, such as S_2 , are accessible after UV absorption (shown in Figure 6.2) which could result in this Coulomb explosion. However, Rolles and coworkers[18] show that there is an ultrafast depopulation of the S_2 to yield ‘hot’ highly, vibrationally excited, electronic ground-state (ring-closed or ring-opened) molecules. It was shown previously that the Channel II yields of these ions remained reasonably unchanged for long pump-probe delays (> 10 ps). This observation suggests that the channel does not derive from a short-lived excited state and rather from the ‘hot’ ground-state molecules.

The decay constants for the Channel II ions of CH_xO^+ and $C_3H_xS^+$ and the Channel I ions in Table 6.1 are all similar (< 500 fs). From the photoexcitation

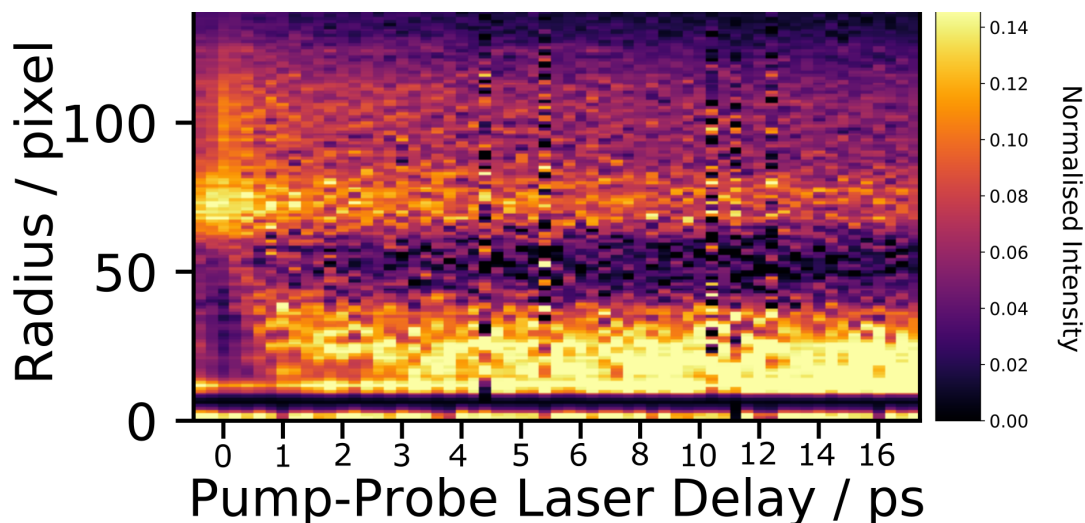


Figure 6.17: Delay-dependent velocity distribution of S^+ ions at a higher UV laser intensity ($I \approx 2 \times 10^{12} \text{ W cm}^{-2}$).

scheme discussed, the products could all derive from the ring-opening of thiophenone with different subsequent fates *i.e.* Coulomb explosion or dissociative ionisation.

6.6 High UV Intensity Dynamics

This section will briefly describe some of the dynamics of the photoexcitation of thiophenone taken at a higher UV laser intensity, ($I = 2 \times 10^{12} \text{ W cm}^{-2}$). As shown earlier, at a higher UV laser intensity, multiphoton absorption results in extensive formation of atomic and molecular ions. As only ions can be detected, it can be assumed that many more neutral atoms are produced from the UV pulse.

Figure 6.17 shows the delay-dependent velocity distribution of sulfur ions under these conditions. The UV pulse dissociates and possibly ionises the sulfur atom. At a delay, Δt , the IR pulse ionises both fragments resulting in a Coulomb explosion. As the delay between the two pulses increases, the interfragment separation increases and a correspondingly weaker Coulomb repulsion is experienced. This is observed in the velocity distribution as a ‘Coulomb’ curve which follows a $1/r$ decay, where r is the separation between the S^+ and a cofragment ion. The onset of the ‘Coulomb’ curve is prompt ($< 0.5 \text{ ps}$). Parts of the velocity distribution are low in quality as

a result of a lack of laser shots comprising the experiment and no mechanism to correct for power fluctuations, however the overall trends are clear.

6.7 Conclusions

In this Chapter, the UV induced photo-excitation dynamics of thiophenone ($\lambda = 267$ nm) was probed by intense IR ionisation in a Coulomb explosion imaging experiment. The dynamics of both ionisation probes have been studied extensively and categorised accordingly. From the observed dynamics, a reasonable mechanism of the photo-excitation has been made with each channel accounted for. Where possible, these channels have been corroborated with covariance analysis to determine ion correlations, specifically for Channel II ions.

Delay-dependent covariance analysis also suggests that a novel Coulomb explosion pathway is observed between the CH_xO^+ and the $\text{C}_3\text{H}_x\text{S}^+$ ions. This, in combination with the Channel II yields for these ions, suggest that the enhancement observed is a result of the increased Coulomb explosion of vibrationally ‘hot’ ring-closed thiophenone and ring-opened isomers. The delay-dependent covariance signature suggests a Coulomb explosion between the two fragments consistent with the ring-opened structure predicted by Murdock *et al.*[234] and Rolles and coworkers[18].

The results gleaned from this UV-IR experiment with limited statistics and an optical laser system that was not always consistent is very promising. This experiment would benefit from further study employing FLO for stable pump-probe experiments at a range of excitation wavelengths under high statistic conditions. This would enable delay-dependent covariances for multiple ion pairs to converge and to categorically understand the Coulomb explosion dynamics involved. The combination of finer pump-probe delay steps and shorter laser pulses would allow for very short timescale dynamics to be recorded and potentially track the ring-opening. The experiment could also go to much longer pump-probe laser delays to look for ion correlations at these delays and determine if signatures of ring-closing could be observed through perhaps an increase in covariance intensity at these delays.

7

The Photochemistry of Thiophenone: 2

7.1 Introduction

This Chapter relates to the dynamics and fragmentation of the UV-excited thiophenone, as discussed in the previous chapter. In this Chapter, the dynamics are probed with XUV photons ($\lambda = 6.3 \text{ nm}$, $E_{h\nu} = 197 \text{ eV}$) from the FLASH FEL, in order to site-selectively ionise at the S(2p) orbital[113], see Section 5.3. The experiments were performed at the Free-electron Laser Facility at Hamburg (FLASH). A detailed discussion of the UV photochemistry of thiophenone was introduced in the previous Chapter. Rolles and coworkers showed that the UV induced ring-opening of thiophenone in the gas phase occurs within 350 fs through time-resolved photoelectron spectroscopy with a seeded XUV pulse[18]

7.2 Experimental Overview

The experimental equipment used in this Chapter is described in great detail in Chapter 2 so a short description will only be provided here. Experiments were performed using the CFEL-ASG multipurpose (CAMP)[93] chamber at DESY during a time-restricted beam-time.

7.2.1 Experimental Set-up

The experimental set-up at FLASH was outlined in the previous Chapter. The only difference to the set-up in the recording of the data in this Chapter is the method of probe pulse, which employs the FLASH FEL rather than the 800 nm fundamental from the in-house Ti:Sa laser. For a detailed discussion on the principles of free-electron lasers refer to Chapter 2. An XUV photon energy of 197 eV was chosen to coincide with absorption cross-section of the S(2p) atomic orbital[113]. This was discussed in more detail in Section 5.3.

7.2.2 Data Correction

The data recorded from experiments using the FLASH FEL must be corrected to account for the fluctuating characteristics of the FEL pulse, *i.e.* pulse energy and BAM correction. Data in this Chapter that required correcting has been done according to the illustrative example outline in Section 2.4.4.

7.3 Experimental Results: FEL Only

This section will discuss the XUV irradiation of thiophenone with the FLASH FEL at 6.3 nm (197 eV).

7.3.1 Time-of-Flight Analysis

The mass spectrum obtained following irradiation of thiophenone with 6.3 nm light from the FLASH FEL is shown in Figure 7.1. The spectra shown are the mass-calibrated time-of-flight spectra obtained from the PImMS camera after centroiding (red) and the analogue-to-digital current (ADC) readout (blue). As discussed in the previous Chapter, the ADC readout has a much greater time resolution (500 ps) than the PImMS2 sensor (25 ns) and is therefore capable of resolving ions with close-lying mass-to-charge ratios, m/z .

The XUV pulse induced extensive fragmentation of thiophenone as evidenced by the prevalence of atomic and lower mass fragment ions. This indicates that the dominant dissociation pathway following the interaction is *via* Coulomb explosion.

The site selectivity of the FEL pulse is also observed in the formation of multiply charged sulfur ions, up to S^{6+} . Large fragments with a $m/z > 50$ are less common than lighter fragments which shows that typically thiophenone undergoes extensive fragmentation.

The greater mass resolution attained by the ADC readout in comparison to PImMS is observed in the inset figure, which shows the respective mass spectra magnified around $m/z \approx 30$, corresponding to the $C_2H_x^+$, CH_xO^+ , S^+ , and $C_3H_x^+$ ions. The mass spectrum obtained from PImMS cannot resolve the $C_2H_x^+$ and CO^+ ions nor the $C_3H_x^+$ ions. However, the mass spectrum obtained from the ADC readout is able to resolve each of these peaks uniquely. Unresolved peaks from the PImMS spectrum are resolved throughout the ADC readout mass spectrum such as the CH_x^+ , the thiophenone dication and the deprotonated structure of the parent and largest fragments. Though in these experiments, velocity information of these resolved ions cannot be extracted from the ADC trace, the total ion yields can be used to study dynamics which the equivalent ion yields extracted from PImMS data is not sensitive to.

7.3.2 Time-of-Flight Covariance

The acquisition of time-of-flight (ToF) spectra for each laser shot from both PImMS and the ADC readout allows for the statistical measurement of correlations between ions appearing in the ToF spectrum through one-dimensional covariance. This was discussed in detail in Section 5.4.1, where ToF covariance[69, 70, 80, 224, 226] was introduced.

As discussed in Section 5.4.1, ToF covariance relies on a stable photon flux from the light source, which is inherently not the case for FELs. The stochastic nature of XUV pulse generation through SASE[101, 108] results in a photon flux or pulse energy that fluctuates on a shot-by-shot basis. More ions are produced for FEL shots of a higher pulse energy and vice versa. The effect of this in the ToF covariance map is artificial correlations between ions appear. To overcome these artificial coincidences, partial covariance mapping was used[69, 80]. Partial

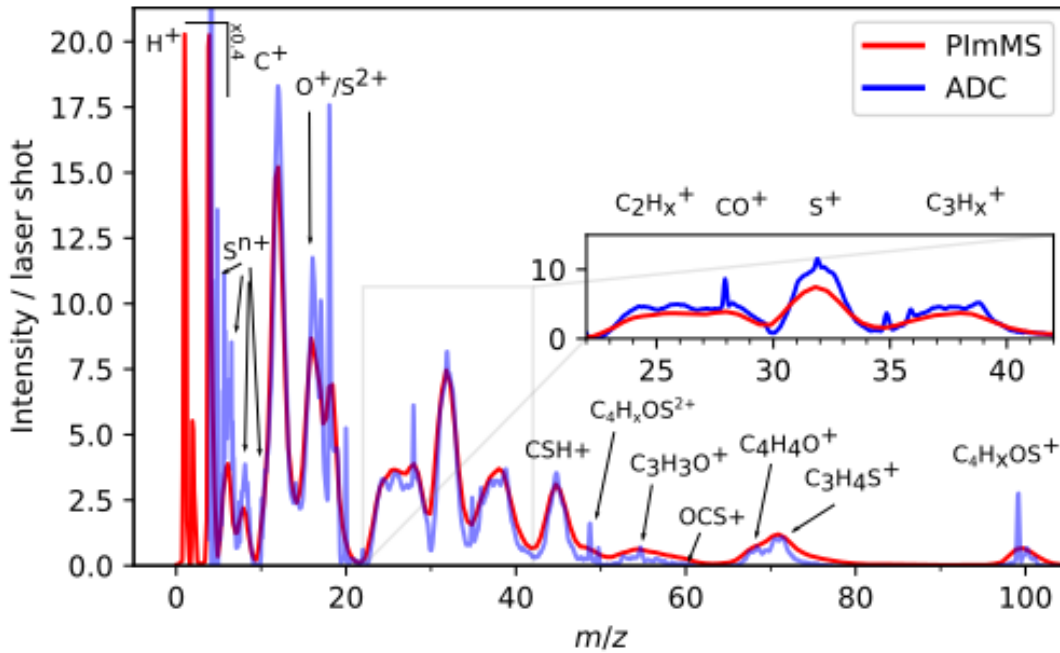


Figure 7.1: The mass spectra for thiophenone after XUV irradiation with the FLASH FEL at 6.3 nm. The red trace shows the mass spectrum obtained from the PImMS camera and the blue trace shows the corresponding spectrum obtained from the ADC readout. Ions are labelled accordingly. The inset shows a magnification of both mass spectra across the mass-to-charge ratio range 22 – 42 to illustrate the increased mass resolution attainable through the ADC readout.

covariance mapping takes into account the fluctuating pulse energy for each shot, and was discussed in Section 5.4.1.

Figure 7.2 shows the partial time-of-flight covariance maps calculated from the ADC ToF spectra. Ion correlations are manifest as lines of intensity in the off diagonal and are borne from conservation of momentum. The times-of-flight of ions formed from the same Coulomb explosion process are correlated as the distribution of momenta and the velocity-mapping conditions are unchanged. As the ToF of an ion is dependent only on the velocity along the ToF axis and the two ion velocities are related through conservation of momentum, the times-of-flight are correlated.

For two species with equal charge formed from a two-body break-up, the ion correlation will appear as a line of gradient -1 at the corresponding ToF intersection. For ion species with a $2 : 1$ charge ratio, the gradients on either side of the diagonal will be $-\frac{1}{\sqrt{2}}$ and $-\sqrt{2}$. In general, for an ion pair in a two-body break-up with

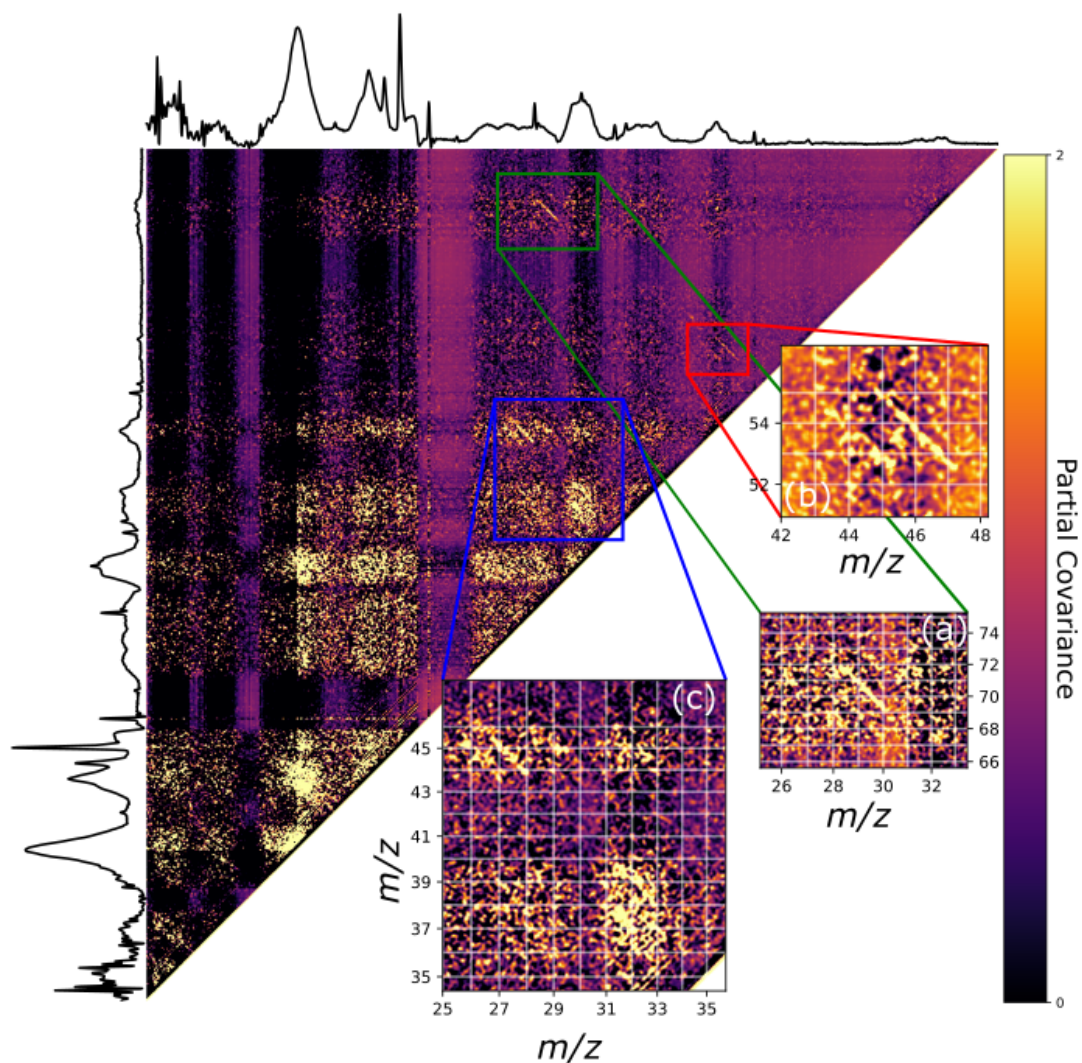


Figure 7.2: Partial time-of-flight covariance map (calculated using Equation (5.6)) from the ToF spectra recorded by the ADC readout. Each axis represents the ion time-of-flight of the ADC trace. The average time-of-flight spectrum is projected on each axis. Insets (a), (b), (c) show individual islands of interest which are discussed in more detail in the text. The axes in the insets are the calibrated mass-to-charge ranges. See text for more details.

a $m : n$ charge ratio in coincidence will present as two lines at the corresponding m/z intersections with gradients of $-\sqrt{\frac{n}{m}}^{-1}$ [237].

The covariance map reveals a number of ion correlations. The highly resolved ToF spectra allow for identification of ions through a mass calibration. The blue inset shows the magnified island for ions with a m/z range from 25 – 33 on the x - axis and 35 – 45 on the y - axis. The correlations along the bottom of the island correspond to S^+ and $C_3H_x^+$ and S^+ and $C_2H_x^+$ ions. The correlations in the top left of this island correspond to CSH_x^+ and ions with a $m/z \approx 27$. The second ion could be $C_2H_x^+$ or $C_2H_2CO^{2+}$. The green inset shows the magnified island for ions with a m/z range from 26 – 30 on the x - axis and 68 – 74 on the y - axis. The two lines correspond to CH_xO^+ and $C_3H_3S^+$ and CO^+ and $C_3HH_xS^+$ ions. The red inset shows the island for the m/z ranges 43 – 47 and 53 – 57 and corresponds to the $C_3H_xO^+$ and CSH_x^+ ion pair.

These ion correlations are investigated further through recoil-frame angular covariance analysis using the relevant PImMS data. Most of the ion correlations discussed relate to ‘true’ two-body break-ups where no other fragment species is involved. Such processes must recoil in opposite directions and should be reflected in the angular covariance with a back-to-back covariance signature.

7.3.3 Angular Covariance

Recoil-frame angular covariance between ions displaying back-to-back recoil are shown in Figure 7.3. A clear covariance signature is apparent in most of the covariance maps at 180° to the reference ion direction. This recoil is expected for ion pairs that sum to the parent molecule, as due to momentum conservation the ions must recoil in opposite directions. The velocity of each covariance signature corresponds to the velocity of the plotted ion as a result of the two-body Coulomb explosion process with the reference ion. The ion pairs that display this recoil are (from top row down) S^+ and $C_4H_4O^+$, CH_xO^+ and $C_3H_xS^+$, $C_3H_xO^+$ and CSH^+ , and $C_3H_x^+$ and OCS^+ . The ion correlations between OCS^+ and $C_3H_x^+$ were not observed in the ToF covariance map (Figure 7.2).

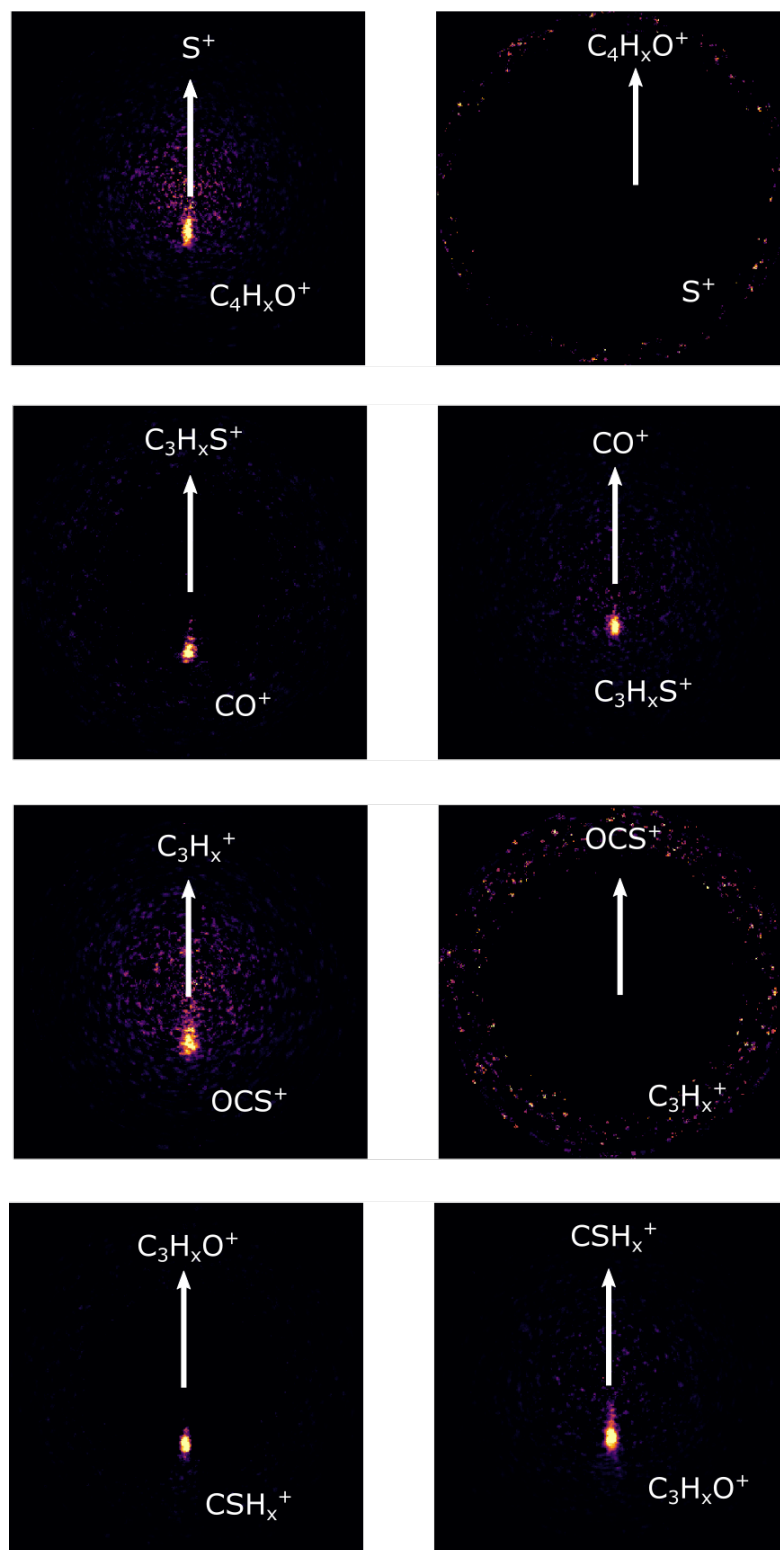


Figure 7.3: Recoil-frame angular covariance maps between ion pairs, displaying back-to-back recoil. Arrow marks the direction of the reference ion recoil, the plotted ion is labelled in the bottom half of each map.

For the covariance maps, $\text{Cov}(\text{C}_4\text{H}_4\text{O}^+, \text{S}^+)$ and $\text{Cov}(\text{OCS}^+, \text{C}_3\text{H}_x^+)$ no covariance was observed despite a clear covariance signature in the reversed covariances (*i.e.* $\text{Cov}(\text{S}^+, \text{C}_4\text{H}_4\text{O}^+)$ and $\text{Cov}(\text{C}_3\text{H}_x^+, \text{OCS}^+)$). This is a result of calculating angular covariance where there are relatively few reference ions in the data. From observing the mass spectra in Figure 7.1, this is the case for both OCS^+ and $\text{C}_4\text{H}_4\text{O}^+$, which are rarely produced ions. The covariance is calculated cumulatively for each reference ion and as there are relatively few ions the covariance does not reach a satisfactory convergence.

Figure 7.4 show the recoil-frame angular covariance maps between the remaining ion pairs observed in Figure 7.2, S^+ and C_3H_x^+ and CSH_x^+ and a second ion X. The identity of X could be either C_2H_x^+ or $\text{C}_2\text{H}_x\text{CO}^{2+}$ from its mass-to-charge ratio. The covariance observed in these ion pairs is much more diffuse than those observed in Figure 7.3 both in radial and angular distribution. This is not unexpected as in each case at least one more fragment must have been also formed (either neutral or charged) from the parent molecule. This fragment must take momentum away from the system and therefore produce a range of momenta that could be shared between the shown fragments.

The covariances in this section have shown that Coulomb explosions channels exist for the FEL only dynamics. These dynamics must be considered when assigning covariance signatures to the pump-probe data.

7.4 Pump-probe Dynamics

7.4.1 Time-of-Flight Analysis

The mass calibrated average ToF spectra recorded by PImMS following irradiation of thiophenone with the FEL pulse ($\lambda = 6.3 \text{ nm}$) (blue) and UV and FEL pulses are shown in Figure 7.5.

As discussed in Subsection 7.3.1, the FEL induces significant fragmentation and ionisation of thiophenone. Data for the UV-FEL mass spectrum was integrated over all pump-probe delays and there is a moderate increase in ion yield observed for most ions. Some of this is a result of the one colour UV signal, specifically

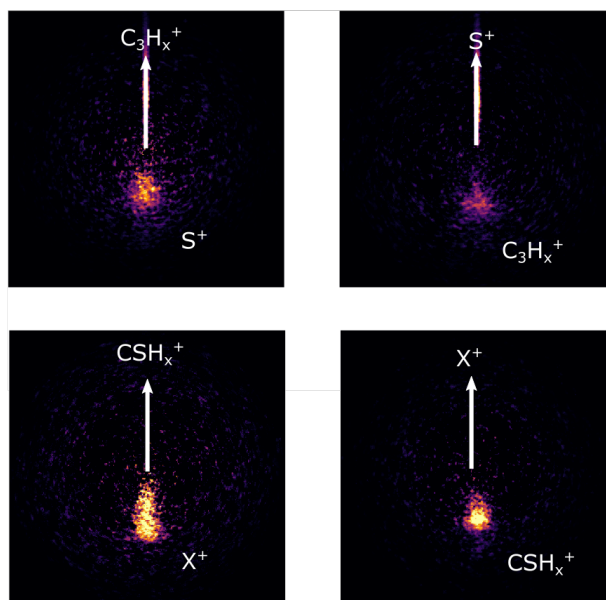


Figure 7.4: Angular covariances between ion pairs observed to be correlated from the ToF covariance in Figure 7.2. The first row shows $\text{Cov}(\text{C}_3\text{H}_x^+, \text{S}^+)$ and the second row shows $\text{Cov}(\text{CSH}_x^+, \text{X})$, where X is an unidentified ion. Arrow marks the direction of the reference ion recoil.

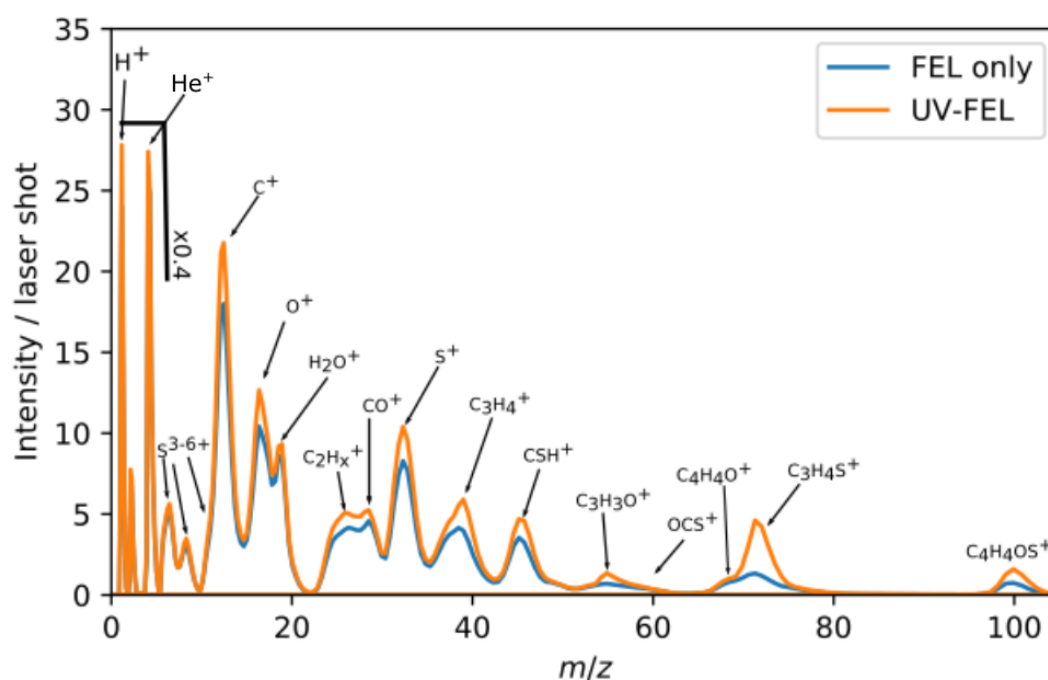


Figure 7.5: The mass spectrum obtained after irradiation of thiophenone with UV and FEL pulses integrated over all pump-probe delays (orange). The mass spectrum obtained after irradiation with just the FEL pulse is shown for reference (blue). Both spectra are normalised to the total number of laser shots.

the increase in the parent and the $\text{C}_3\text{H}_x\text{S}^+$ ions (see UV only mass spectrum in Figure 6.4). The observed enhancement in the smaller fragments and atomic ions are a result of UV-XUV photo-excitation dynamics.

7.4.2 Ion Image Analysis

This section will explore the effect that a UV photon has on the VMI ion images as a function of pump-probe delay and UV pulse energy. As discussed in Section 7.4.1, there are few absolute changes in the total ion yields at pump-probe delays relative to the FEL-only data.

The PImMS camera enables analysis of the velocity dependence of the recorded ions to be measured which may behave differently to the overall ion yield. Ions are differentiated by ToF and an ion image for each delay bin is created. This image is then four-fold symmetrised and normalised to the total FEL power comprising the delay bin and inverted to obtain the distribution of the three-dimensional velocity distribution.

Experiments were performed over a range of delays from -2 to $+4$ ps, relative to temporal overlap, t_0 , where positive delays correspond to delays where the UV laser pulse precedes the FEL pulse and vice versa. The shot number recorded by PImMS is correlated to the FLASH DAQ system such that information pertaining to a specific shot can be assigned to each PImMS shot data set. These include the Bunch Arrival Monitor, the pulse energy, and the streak camera delay. These parameters were discussed in Section 2.4.4 and allow for more accurate pump-probe delay assignment and normalisation by total FEL power. PImMS (x, y, t, s) data recorded over all pump-probe delays were collated and subsequently corrected for the corresponding BAMs. The new corrected delays were then re-binned into pump-probe delay bins of 100 fs.

In this section, two data sets will be investigated. Firstly, the UV photoexcitation dynamics at a pulse energy of approximately $9\mu\text{J}$ comprising 115,000 laser shots. Secondly, experiments performed at a lower pulse energy of approximately $1\mu\text{J}$, comprising 136,000 laser shots will be discussed.

High UV Intensity

Figure 7.6 shows the delay-dependent velocity distribution ((a), (b) and (c)) of the inverted S^{n+} , ion images, ($n = 2 - 4$). The UV Early, pump-probe delays where the UV pulse arrives before the XUV pulse (red), and the UV Late, where the UV pulse arrives after the XUV pulse, (blue) projections of the velocity distribution are plotted on the right of each heatmap. Various channel ion yields are shown in the right column (Panels (d)-(i)). The corrected pump-probe delays have been offset such that 0 ps corresponds approximately to the temporal overlap of the UV and XUV laser pulses.

Each velocity distribution heatmap bears similarities. The most distinct similarity is the strong enhancement to low kinetic energy ions at pump-probe delays of $t > 0$ ps (*i.e.* after UV absorption). This enhancement is accompanied by a curve in the intensity. Similar so-called ‘Coulomb curves’ have been reported previously in alkyl halides such as CH_3I and CH_2ClI [58, 59, 61, 238]. The cause of the ‘Coulomb’ curve was discussed in Chapter 2 and corresponds to the dissociative ionisation of thiophenone and to form a sulfur and a cofragment, X^+ . The sulfur atom is subsequently multiply ionised by the XUV pulse[113] and induces a Coulomb explosion with X^+ . The kinetic energy release (KER) of the Coulomb explosion is dependent on the intercharge separation. This distance is dependent on the pump-probe delay as this length of time determines how far separated the fragments are at the moment of Coulomb explosion. Thus at longer pump-probe delays, there is a smaller additional Coulombic energy and a lower KER sulfur ion is observed. The ion yields for this channel is shown in the orange trace in the right column. Recoil-frame angular covariance was attempted to determine which ion or ions corresponded to X^+ . However, no correlations were observed. This could be a result of too few laser shots in this dataset. The corresponding channel yields are shown in Panels (d)-(f) (blue crosses) and were fit to the convoluted exponential function in Equation (2.4) (red dashed line). Each ion had an exponential rise time of 0.5 ps.

Secondly, there is an observed depletion in the yield of high KER ions as shown in Panels (g)-(i). This is a result of the general fragmentation of thiophenone

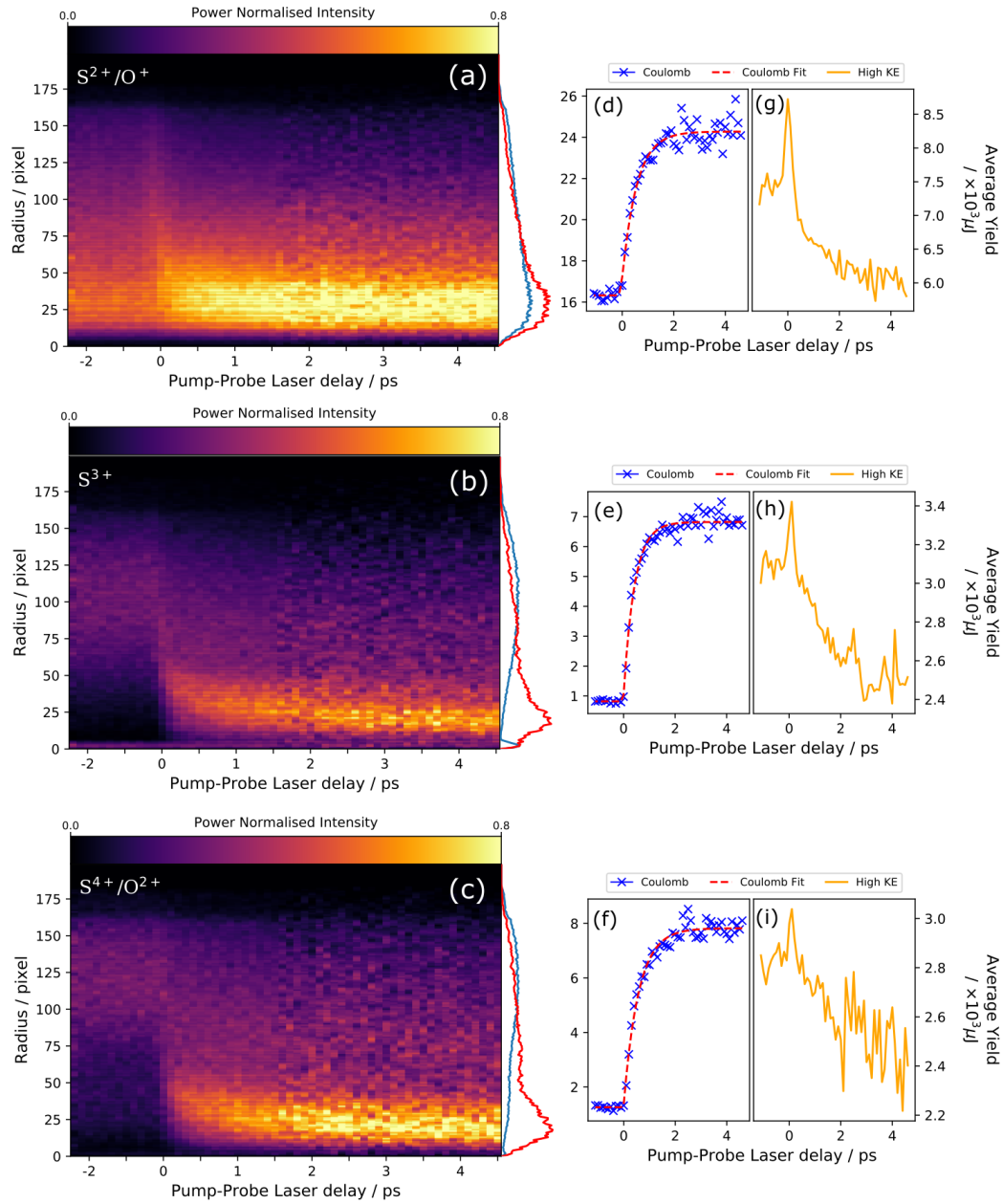


Figure 7.6: UV-XUV photoexcitation dynamics of S^{2+}/O^+ (top row), S^{3+} (middle row), and S^{4+}/O^{2+} (bottom row). Panels (a)-(c): The delay-dependent radial distributions of multiply charged sulfur ions. Panels (d)-(i): delay-dependent channel yields for each ion.

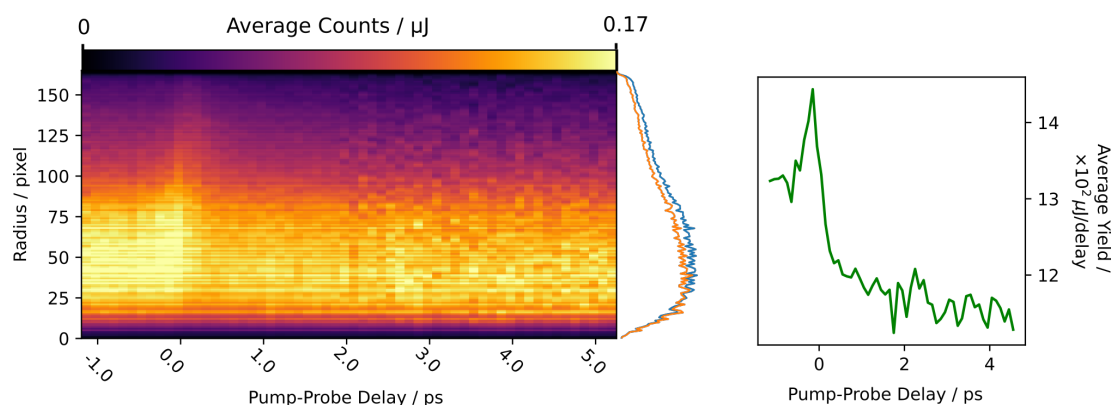


Figure 7.7: UV-XUV photoexcitation dynamics of C^+ . Left: delay-dependent radial distribution map; right: delay-dependent yield integrated across all radii.

after the UV pulse and shows that much fewer parent molecules are left intact. After the fragmentation, the remaining fragments are further apart and therefore fewer ions with a high KER are produced. This depletion is accompanied by an enhancement at t_0 .

Figure 7.7 shows the analogous distribution for C^+ ions to demonstrate that similar dynamics were observed in ions across the ToF spectrum. Again, a decrease in yield for ions with a high KER was decreased, following an enhancement in yield around t_0 .

All the dynamics that have been discussed in this Section derive from multiphoton UV absorption. Therefore at these UV pulse energies, the majority of the ion channels correspond to a dissociation of thiophenone rather than an isomerisation. It is probable that some thiophenone has undergone ring-opening, however, the dynamics are clearly dominated by multiphoton dissociation.

Low UV intensity

This section will outline and discuss the UV pump- FEL probe dynamics of thiophenone at a UV pulse energy of $\approx 1\mu\text{J}$ ($I \approx 3 \times 10^{11} \text{ W cm}^{-2}$). The UV only dynamics at these intensities were discussed in detail in Section 6.3.1. It was established that at these UV intensities multiphoton absorption was suppressed and that single photon absorption was the dominant interaction. As discussed in the previous Chapter, thiophenone is known to ring-open and subsequently

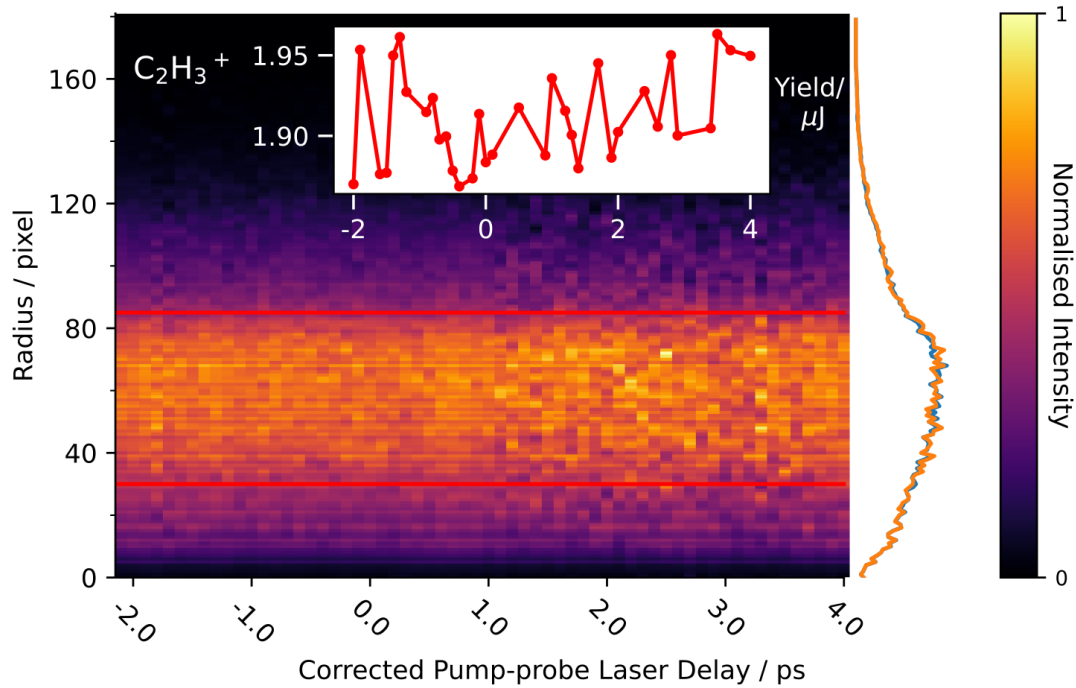


Figure 7.8: The delay-dependent velocity distribution of the C_2H_x ions.

isomerise upon absorption of a UV photon at 267 nm[18, 234] forming a number of photoproducts.

Many ions are present in the ToF spectrum and not all will be discussed in this section as most ion velocity distributions are delay independent and do not require a detailed discussion. This suggests that either the XUV laser pulse dominates the effects observed in these experiments or the UV pulse affects the velocity distributions in subtle ways leading to very small changes in the distribution. This is not unexpected as the role of the UV photon was to initiate an isomerisation. One such ion will be shown here as an example.

Figure 7.8 shows the delay-dependent radial distribution for the C_2H_x^+ ions. For clarity, negative (positive) pump-probe laser delays correspond to UV late (early) delays where the UV laser pulse precedes (succeeds) the FEL pulse.

The UV late (blue) and UV early (orange) projections of the velocity distribution are shown on the right edge of the radial distribution. These were calculated by averaging the intensity along the radial axis for the first and last 1000 fs of the data set. These distributions are indistinguishable. The features present here can

be assumed to be dominated from a Coulomb explosion process from the FEL pulse only. The radial range corresponding to the peak of the image is marked by two red horizontal lines and the delay-dependent ion yield is plotted in the inset. There is no clear change in the ion intensity (normalised to the total laser power) over the delay range.

The left column of Figure 7.9 shows the radial distributions of inverted images of sulfur ions with increasing charge, S^{n+} . Sulfur has twice the mass of oxygen and it is therefore impossible from ToF analysis alone to distinguish between O^{n+} and S^{2n+} ions. The velocity distributions for the mass-to-charge ratios corresponding to O^+/S^{2+} and O^{2+}/S^{4+} are the sum of both ion velocity distributions. Due to the relative atomic absorption cross-section at the current photon energy (197 eV), it is unlikely that much O^{2+} was produced (and even less O^{4+})[113]. However O^+ is readily produced as the result of Coulomb explosion. The O^+ and S^{2+} radial distribution is approximately bimodal with two broad peaks centred at ≈ 30 and ≈ 100 pixels, respectively. The O^+ can be qualitatively distinguished from the S^{2+} as the lighter ion would be expected to have a greater KER than the heavier sulfur and multiply charged ions are more tightly mapped in VMI conditions. The two regions are marked as red and blue horizontal lines. However, the two peaks are not distinct and it is likely that higher energy S^{2+} exist in the blue region. The blue plot and first red plot on the right column show the delay-dependent ion yield of these ions. Both show an increase in yield of around 10%, relative to the UV late yield.

The timing resolution of PImMS introduces some ambiguities in the ion ToF windows and resultantly the ion images. Firstly, the ToF range corresponding to the S^{3+} ion ($m/z = 10.7$) partially overlaps with the C^+ ion ($m/z = 12$) in the PImMS ToF spectrum which will affect the velocity distribution. Secondly, the S^{5+} and $S^{6+}(/O^{3+})$ are unresolvable and have therefore been grouped together as the sulfur ion images should be qualitatively similar.

The velocity distributions of the more highly charged cations all display similar features and are analogous to the equivalent plots shown at higher UV pulse energies in Figure 7.6. Firstly, the peak at high radii in the velocity distribution shifts to

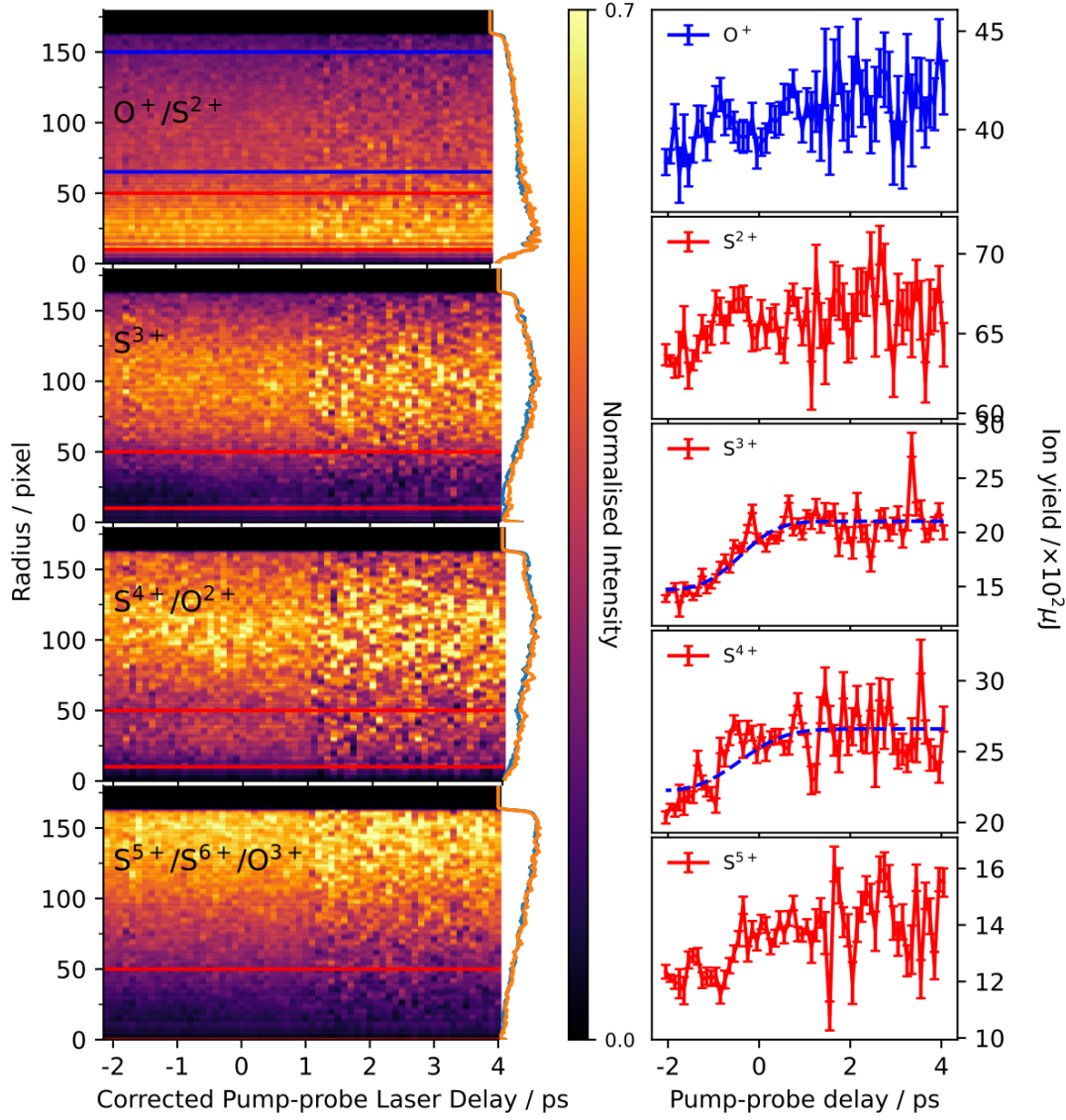


Figure 7.9: Left: Delay-dependent radial distributions of inverted images of the S^{n+} ions ($n = 2 - 6$ from top to bottom). Right: delay-dependent ion yields for the radial regions in the heatmaps. Exponential fits are also shown for the S^{3+} and S^{4+} ions.

higher radii as the charge is increased. This is expected as the KER of the ions is related to Coulomb's Law and therefore increases with increasing charge.

Secondly, an enhancement in low velocity ions is observed, notably in the S^{3+} and S^{4+} ions. This feature is far less dominant ($\approx 10\times$ weaker) than was observed in Figure 7.6 at higher UV pulse energies. The enhancements in these ions are observed in the UV- early and late velocity distribution comparison. The 'Coulomb curves' are not observed as clearly at these UV intensities as this is a relatively weak

channel in comparison with the Coulomb explosion of the intact molecule. The fact that this channel is weak is encouraging as it suggests that the UV laser intensity is such that multi-photon absorption is not prevalent and is in the single-photon regime. These enhancements are shown in the corresponding delay-dependent ion yields in the right column of Figure 7.9. Convoluted exponential functions (Equation (2.4)) have been fit for the S^{3+} and S^{4+} ions and are plotted in the right column (blue). The exponential rises for these ions are ≈ 0.5 ps, in agreement with the equivalent dynamics observed at higher laser intensities in Figure 7.6.

Figure 7.10 shows the delay-dependent velocity distributions of the S^+ (top), C^+ (middle), and CH_xO^+ (bottom) ions. Delay-dependent ion yields are shown in the right column, for the radial ranges marked in the corresponding heatmap. For the S^+ ion, the dominant feature in the velocity distribution corresponds to a Coulomb explosion process at 70 pixels. The broadness of this peak shows that sulfur is borne with a range of KERs as a result of many different Coulomb explosion processes that produce it. This channel is dominated by the FEL pulse and any UV delay-dependence would be small. This is evident in the ion yield which does not show a significant delay dependence.

The C^+ ion also displays a very broad velocity distribution. This is further indicative of the number of Coulomb explosions that are possible as a result of thiophenone interacting with the FEL pulse. This is intensified as there are four carbon atoms at unique positions which can each be ionised individually. This greatly increases the spread of KERs that an ion can be produced with which is observed here. This channel does show an enhancement at UV early delays.

The CH_xO^+ velocity distribution has a peak at between 50 and 70 pixels. This has already been partially attributed to a BTB Coulomb explosion with $C_3H_xS^+$. However, the angular covariance of this Coulomb explosion process implied a sharp velocity distributions which is not observed here. This suggests that CH_xO^+ ions in this channel are also borne from other Coulomb explosion processes which necessarily introduce the broadness into the velocity distribution.

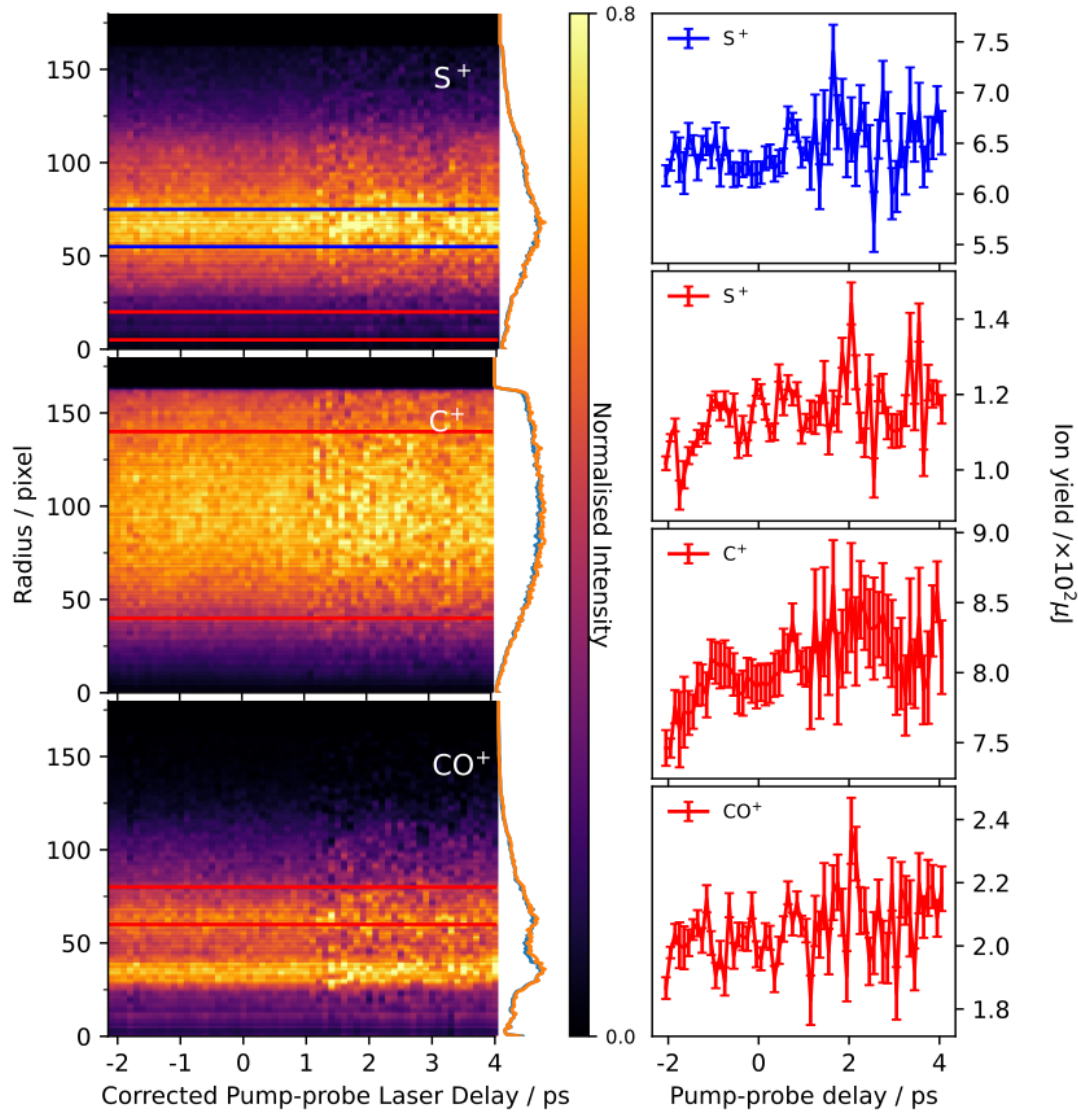


Figure 7.10: Delay-dependent radial distributions of inverted images of the S^+ , C^+ , and CO^+ ions (from top to bottom). UV Early and Late projections are shown on the right of each heatmap. Delay-dependent velocity channels are shown for each ion in the right-hand column.

7.4.3 Time-of-Flight Covariance

This section will investigate the calculated covariance of the ToF spectra recorded by the ADC readout for all pump-probe delays. Figure 7.11 shows the partial covariance ToF-ToF map calculated from 800,000 laser shots for a ToF range corresponding to a m/z range from 12–72 (C^+ to $C_3H_4S^+$), integrated over all pump-probe laser delays.

The covariance map is rich in ion correlations that were either not present in

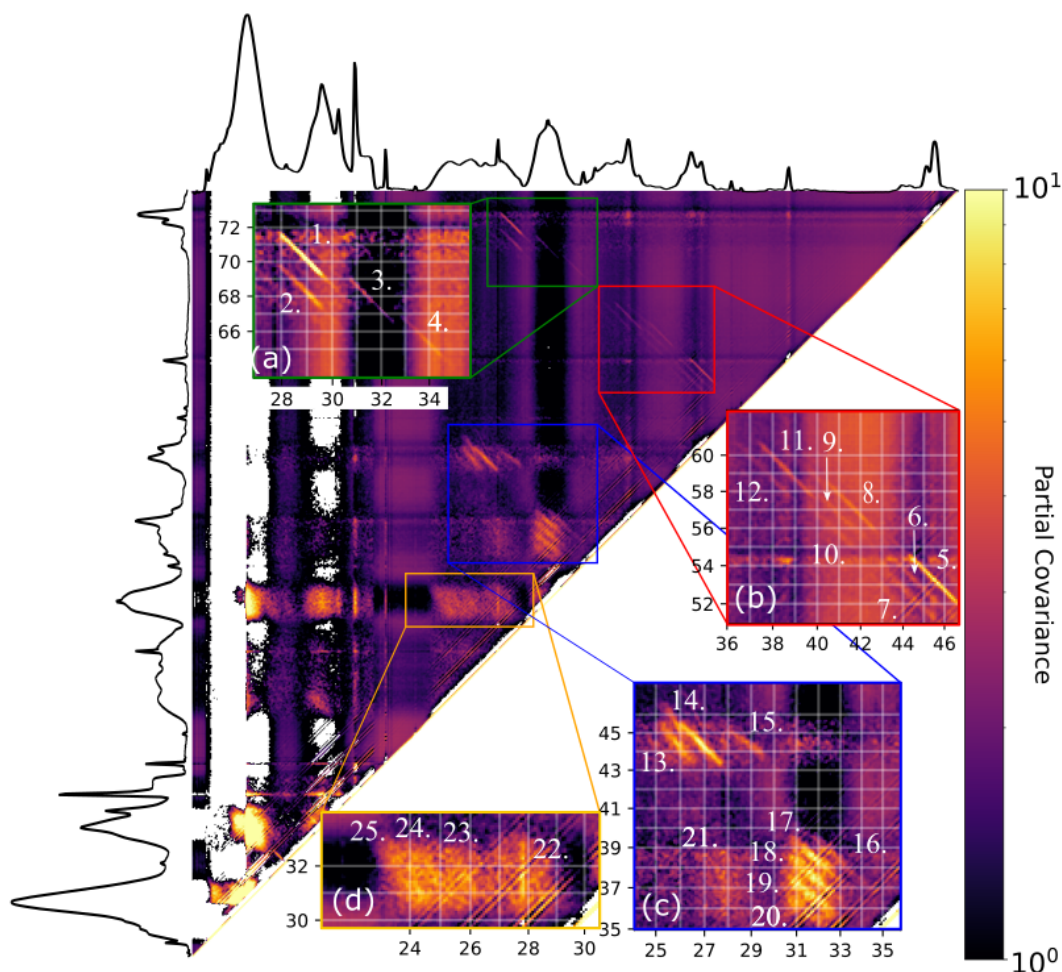


Figure 7.11: Partial ToF-ToF covariance map as recorded by the ADC readout. Data integrated over all pump-probe delays. Specific islands are magnified in the insets, (a)-(d). Covariances corresponding to ion correlations are labelled “1” through “25”. Insets have been labelled with corresponding m/z values with a colour scale to show the correlations more clearly. See text for more details and Table 7.1 for a summary of these correlations.

the FEL only data or not converged due to the relatively few number of laser shots comprising the data set (65,000 laser shots). Figure 7.11 shows one half of the covariance map as the correlations are reflected in the diagonal. Four islands of the covariance map are labelled and display a number of ion correlations within. Each region is magnified in the other half of the Figure to more clearly show the covariance signatures.

The green region, magnified in inset (a) shows the island corresponding to the m/z range of 27 – 35 and 65 – 73. Ion correlations marked 1 and 2 correspond

to the CHO^+ in covariance with the $\text{C}_3\text{H}_3\text{S}^+$ and C_3HS^+ ions. This is interesting as it suggests that it is the CHO^+ ion and not the CO^+ ion that is produced by the FEL pulse. Secondly, it is notable that two ion channels exist for CHO^+ and that no or negligible channels exist for the other protonated $\text{C}_3\text{H}_x\text{S}^+$ ions. These ion correlations were observed in the FEL only ADC ToF covariance and also in the angular covariance observed by PImMS. However, the clarity is much better in the integrated pump-probe data. Ion correlation 3 corresponds to the S^+ ion in covariance with the $\text{C}_4\text{H}_4\text{O}^+$ ion. This correlation was not observed in the FEL only ToF covariance map. However back-to-back angular covariance was observed from the PImMS data. Ion correlation 4 suggests a back-to-back recoil between ions with a m/z of 34 and 66. These mass-to-charge ratios suggest that the ions are SH_2^+ and $\text{C}_4\text{H}_2\text{O}^+$. This is a surprising ion pair as the sulfur atom is not directly bonded to any protons in thiophenone. Therefore, this correlation implies that sulfur combines with two hydrogen atoms during the photodissociation of thiophenone before Coulomb exploding with the $\text{C}_4\text{H}_2\text{O}^+$. This is a relatively weak channel in comparison with the other features in the green-boxed region though reveals a new dissociation pathway of thiophenone. The SH_2^+ is barely resolved in the ADC readout and is only revealed through ToF covariance. Similar ultrafast hydrogen migrations have been observed before in Coulomb explosion studies of acetonitrile[239], methanol[240, 241], and allene[242].

The red region, magnified in inset (b), shows the island corresponding to a m/z range of 36 – 48 and 52 – 62. Ion correlations in the inset are labelled 5 through 12. These ion correlations correspond to back-to-back recoils between a number of ion pairs. The most dominant channels are between the CSH_x^+ and $\text{C}_3\text{H}_x\text{O}^+$ ions (5 – 7). Minor channels exist between CH_xCO^+ and $\text{C}_2\text{H}_x\text{S}^+$ ion pairs (8 – 10). Channels 11 and 12 correspond to a correlation between OCS^+ and C_3H_3^+ and C_3H_2^+ ions, respectively. Most of these ions are very minor peaks in the ToF spectrum and yet show very strong correlations.

The blue region, magnified in inset (c), shows the island corresponding to a m/z range of 25 – 35 and 35 – 46. Ion correlations in the inset are labelled 13 through 21.

Label	Ion 1	Ion 2	$(m/z)_1$	$(m/z)_2$
1	CHO ⁺	C ₃ H ₃ S ⁺	29	71
2	CHO ⁺	C ₃ HS ⁺	29	69
3	S ⁺	C ₄ H ₄ O ⁺	32	68
4	SH ₂	C ₄ H ₂ O ⁺	34	66
5	C ₃ H ₂ O ⁺	CSH ₂ ⁺	54	46
6	C ₃ HO ⁺	CSH ⁺	53	45
7	C ₃ HO ⁺	CS ⁺	53	44
8	CH ₂ CO ⁺	C ₂ H ₂ S ⁺	42	58
9	CHCO ⁺	C ₂ HS ⁺	41	57
10	CHCO ⁺	C ₂ S ⁺	41	56
11	OCS ⁺	C ₃ H ₃ ⁺	60	39
12	OCS ⁺	C ₃ H ₂ ⁺	60	38
13	CSH ⁺	C ₃ O ²⁺	45	26
14	CSH ⁺	C ₃ H ₂ O ²⁺	45	27
15	CHO ⁺	CSH ⁺	29	45
16	S ⁺	C ₃ H ₄ ⁺	32	40
17	S ⁺	C ₃ H ₃ ⁺	32	39
18	S ⁺	C ₃ H ₂ ⁺	32	38
19	S ⁺	C ₃ H ⁺	32	37
20	S ⁺	C ₃ ⁺	32	36
21	C ₃ H _x ⁺	CO ⁺	37-40	28
22	S ⁺	CO ⁺	32	28
23	S ⁺	C ₂ H ₃ ⁺	32	27
24	S ⁺	C ₂ H ₂ ⁺	32	26
25	S ⁺	C ₂ H _x ⁺	32	24-25

Table 7.1: Table summarising the ion correlations observed in the ToF-ToF covariance map shown in Figure 7.11

The ion correlations marked 13 – 14 corresponds to an ion pair with mass-to-charge ratios of 45 and 26 and 27, respectively. The gradient of these lines are $-\frac{1}{\sqrt{2}}$. This suggests that one of the ions is doubly charged. The only ion pair that satisfies this condition are CSH⁺ and C₂H_xCO²⁺. This is not an expected ion pair as the FEL pulse is more likely to ionise at the sulfur[113] and it would therefore be sulfur that would hold more charge. The opposite is true for this correlation. This lack of site-selectivity has been observed in XUV experiments previously[243].

Ion correlation 15 corresponds to ions with mass-to-charge ratios of 45 and 29. This appears to relate to the CSH⁺ and CHO⁺ ion pair though the gradient of the line is neither -1 or $-\frac{1}{\sqrt{2}}$. The exact gradient of the line arises from conservation of

momentum and as this ion pair is at least a three-body break-up it could be possible.

The ion correlations 16 – 20 correspond to S^+ and the C_3^+ and $C_3H_x^+$ ions. This shows that the sulfur ion is formed with each of the $C_3H_x^+$ ions as a result of different Coulomb explosion processes. This detail is lost from the data recorded by PImMS which cannot resolve the individual mass peaks. This could partially explain the broad angular covariance calculated between these ions as PImMS is calculating correlations between the sulfur ion and five distinct ions at once.

The ion correlation marked 21 shows a diffuse correlation corresponding to $C_2H_x^+$ and CH_xO^+ ions. The broadness of this correlation suggests that this is a sum of many multi-body break-ups resulting in a blurred covariance with no distinct features.

The orange region, magnified in inset (d), shows the island corresponding to a m/z range of 24 – 30 and 30 – 33. Ion correlation 22 corresponds to S^+ and CH_x^+ ions. Ion correlations 23 – 25 correspond to S^+ ions and $C_2H_x^+$ and CH_xO^+ ions.

The ion correlations are summarised in Table 7.1. This section has revealed a large number of ion correlations in the data integrated over all pump-probe delays. The high statistic data set allows for a reliable convergence of covariances. It is difficult to ascertain if the observed new ion correlations relative to the FEL only data are pump-probe features or had simply not converged previously, due to a lack of statistics.

Photoion–photoion coincidence data

To assist with identifying all the ion correlations in Figure 7.11, photoion–photoion coincidence (PIPICO) data received from collaborators (Pathak & Rolles, private communication) has been used. PIPICO and PEPICO (Photoelectron–Photoion Coincidence) experiments record ions (and electrons) in coincidence at very low count rates and very high repetition rates. Coincident maps of these events can determine dissociation mechanisms[244–251], kinetic energy releases of nascent ions[244, 251–255], and dissociation rates[251, 256–258].

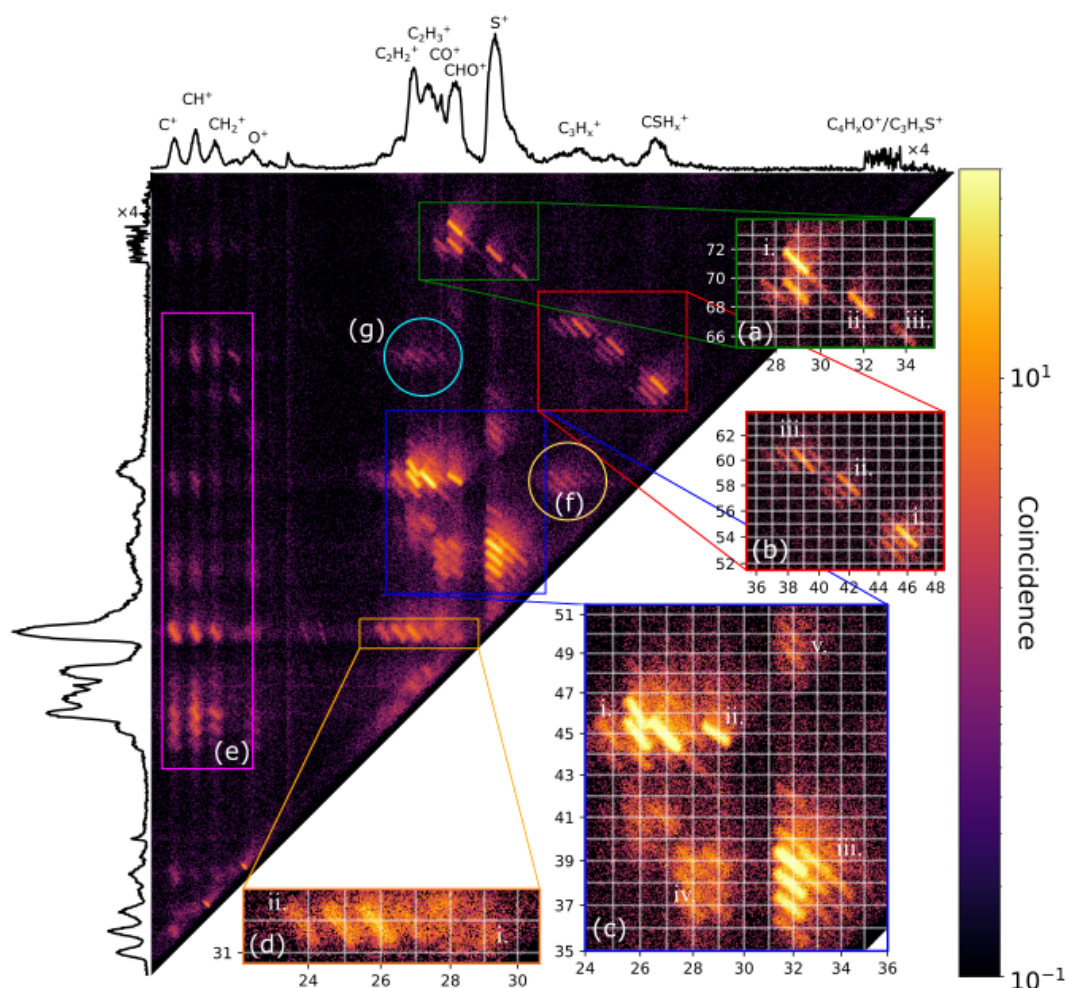


Figure 7.12: Ion time-of-flight coincidence map following PIPICO experiments on thiophenone at a photon energy of 180 eV. Insets (a)-(d) show magnified equivalent PIPICO islands to those in Figure 7.11. Related ion correlations for each island are labelled and can be compared to equivalent correlations in Figure 7.11. Regions (e)-(g) highlight PIPICO islands not observed in Figure 7.11. Insets have been labelled with corresponding m/z values. See text for details.

This data was recorded at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory using a double-sided VMI spectrometer[259]. In these experiments, thiophenone was irradiated with synchrotron radiation with a photon energy of 180 eV. This is a comparable photon energy to that produced by the FLASH FEL in the present work. There is little difference in the cross-sections between these photon energies[113] so it is likely that the coincidence map would be very similar at the slightly higher photon energy that was used at FLASH. This

data can be used as a comparison to FEL only data using the FLASH FEL. The key difference between the two experiments is the XUV peak intensity. The XUV pulse produced by the FLASH FEL has a peak intensity that is much greater than the synchrotron used at ALS and therefore there should be many more multiple XUV photon effects for the FLASH data.

The resultant ToF coincidence map is shown in Figure 7.12 and can be compared to the ToF covariance map shown in Figure 7.11. As discussed in Chapter 5, coincidence and covariance maps are not expected to be identical, however, the covariance map should converge on the coincidence map, under exact photon conditions. The two maps are very similar and share a majority of ion correlations. The PIPICO islands, shown in insets (a) and (b), correspond perfectly with the insets (a) and (b) of Figure 7.11, respectively. These correlations correspond to two-body break-ups of thiophenone. The ion correlations, labelled i., in Panel(a) of Figure 7.12 correspond to the Coulomb explosion pathways:



and are analogous to ion correlations 1 – 2 in Figure 7.11. Similar comparisons can be made for the ion correlations ii-iii and 3 – 4 in the respective Figures.

The PIPICO island shown in inset (c) corresponds to the inset (c) of Figure 7.11 and are also in excellent agreement. From the covariance data, reliable identification of the ion correlations was difficult due to degenerate mass-to-charges, especially those in the top-left corner of the inset, (i. and ii.). The coincidence data can elucidate these ion correlations from the velocity information. The ion correlations are identified as:



The ion correlations labelled iii. are identical to those labelled 16 – 20 in Figure 7.11. The ion correlations labelled iv. and v. are identified as:



These ion correlations were not observed in the covariance data.

Inset (d) shows ion correlations between S^+ and C_2H_x^+ ions. These are comparable to inset (d) in Figure 7.11 and are in excellent agreement. Islands labelled (e) through (g) are marked on the PIPICO map. These correlations were not observed in the covariance map in Figure 7.11. Island (e) corresponds to a number of correlations between CH_x^+ and O^+ with molecular ions across the ToF spectrum. Islands (f) and (g) correspond to a number of weak correlations identified as:



These are similar to ion correlations 5 – 10 in Figure 7.11 except with an oxygen excluded.

7.4.4 Angular Covariance

Recoil-frame angular covariance was also employed to determine the relative momentum of the ion correlations that have been identified through ToF covariance. Covariance maps integrated over all pump-probe delays will first be investigated.

Figure 7.13 shows the recoil-frame angular covariance maps for the ion pairs that were observed to have back-to-back recoil in the FEL only data. This recoil behaviour is observed in these data too and is not unexpected as these ion pairs sum to form the parent molecule. As discussed earlier, the covariance maps where $\text{C}_4\text{H}_4\text{O}^+$ and OCS^+ are the reference ions do not show any covariance and this is a result of there being far fewer reference ions than plotted ions.

From the high resolution ToF covariance data, it is known that these ion pairs are actually a sum of a number of ion pairs. For example the top row, $\text{Cov}(\text{C}_3\text{H}_x\text{S}^+,$

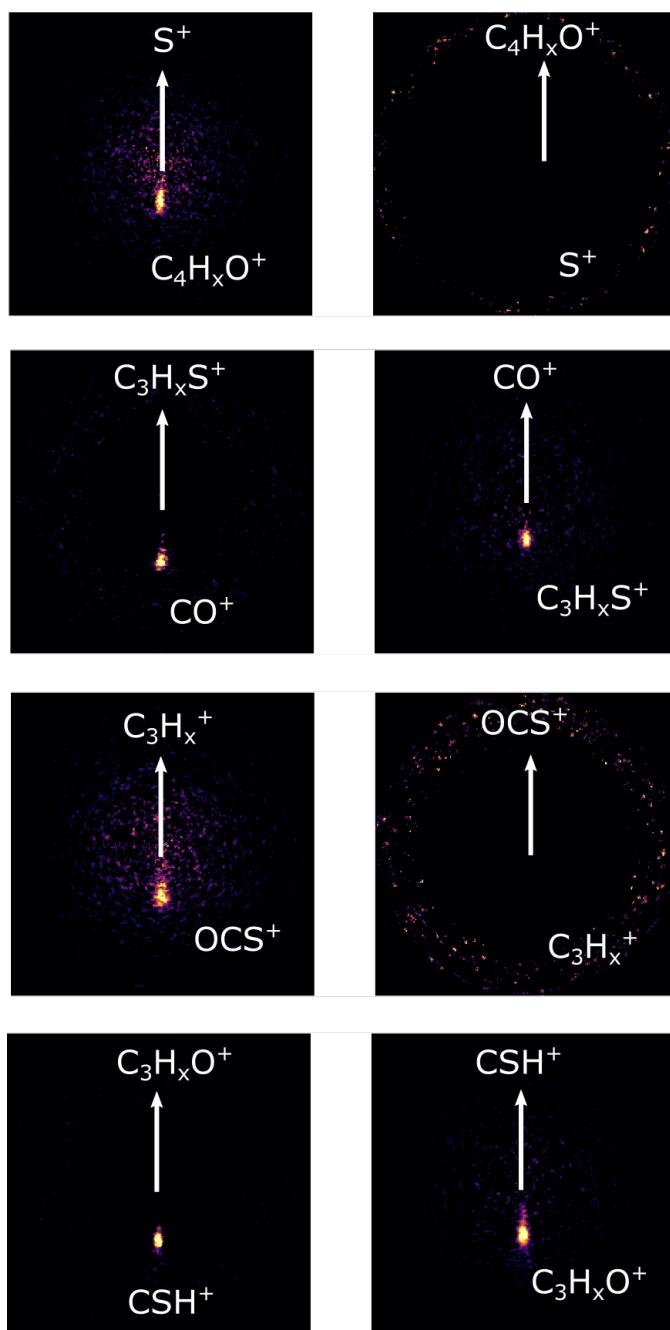


Figure 7.13: Recoil-frame angular covariance maps between ions displaying a back-to-back recoil. Reference ion is labelled along with its direction (up the page). Ion pairs from top row downward: $\text{C}_3\text{H}_x\text{S}^+/\text{CHO}^+$, $\text{CSH}^+/\text{C}_3\text{H}_x\text{O}^+$, $\text{C}_3\text{H}_x\text{O}^+/\text{S}^+$, $\text{C}_3\text{H}_x^+/\text{OCS}^+$.

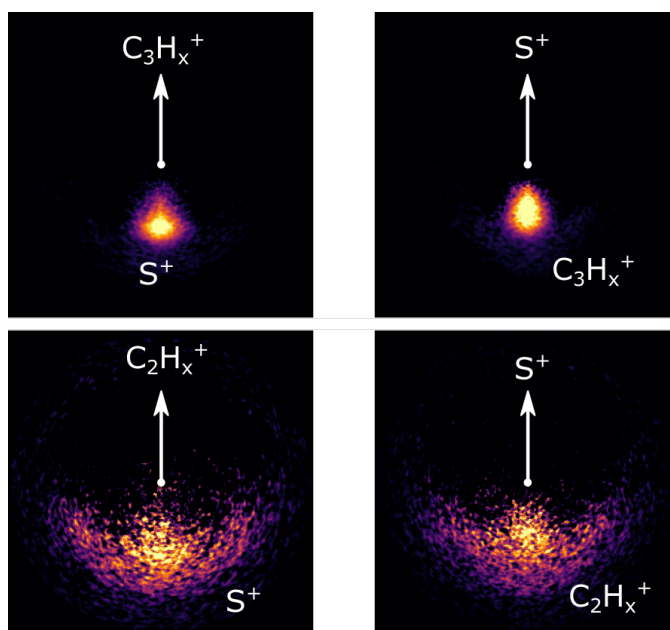


Figure 7.14: The recoil-frame angular covariance maps for the ion pairs: $S^+/C_3H_x^+$ (top row); and $S^+/C_2H_x^+$. Reference ion and direction are labelled.

CHO^+) and $Cov(CHO^+, C_3H_xS^+)$ contains contributions from C_3HS^+ and $C_3H_3S^+$. Similarly, in the third row, $Cov(C_4H_4O^+, S^+)$ and $Cov(S^+, C_4H_4O^+)$ also contains contributions from SH_2^+ . These summed covariances should result in a poorer resolution however the effect is expected to be small and is not observed.

Figure 7.14 shows the corresponding recoil-frame angular covariance maps for the $S^+/C_3H_x^+$ (top row) and $S^+/C_2H_x^+$ (bottom row) ion pairs. $Covs(S^+, C_3H_x^+)$ show a general back-to-back recoil with a larger angular spread than the ion pairs displayed in Figure 7.13. This is expected as there is a CH_xO fragment absent from the dissociation pathway which will take some momentum from the molecular break-up. This results in a recoil that is not completely 180° from the reference ions. This ion correlation was also observed in the FEL only data so this is not a new pump-probe correlation though could have seen an enhancement. The increased radial spread of the covariance signature (relative to the ion pairs in the previous Figure) could be a result of the covariance map being an average of the ion correlations between S^+ and each of the $C_3H_x^+$ ions.

$Covs(S^+, C_2H_x^+)$ again show a broad back-to-back covariance though much weaker than in the previous ion pair. There is a much broader angular distribution to the

covariance maps than in the previous ion pair. This suggests that these ions and the third fragment typically recoil in opposite directions to each other. This results in a relative recoil between these ions that is not 180° . It is also indicative of the large number of Coulomb explosions that lead to the formation of these ions.

Figure 7.15 shows the recoil-frame angular covariance maps for the C_3H_x^+ and S^{n+} ions. Figure 7.14 showed the ion correlations between C_3H_x^+ and S^+ which were larger back-to-back with a slight angular distribution. Figure 7.15 shows the results of the covariance with multiply charged sulfur ions (and/or oxygen ions). As the yield of sulfur ions decreases with increasing charge state, the covariance maps become worse in quality. However, there is enough information in the covariance map to obtain information. Panels a) and b) shows $\text{Cov}(\text{O}^+/\text{S}^{2+}, \text{C}_3\text{H}_x^+)$ and $\text{Cov}(\text{C}_3\text{H}_x^+, \text{O}^+/\text{S}^{2+})$, respectively. These covariance maps show a tendency to recoil in opposite directions. This is not as clear as in previous examples as a result of the noise. This observation is portrayed in Panel c) as the radial integration of the covariance maps in a) and b). Here, the covariance in each map has been integrated over the relevant radial range and plotted against angle, θ , where π corresponds to back-to-back recoil. It is clearer that these ions typically recoil in opposite directions. Panels c) and d) show $\text{Cov}(\text{C}_3\text{H}_x^+, \text{S}^{3+})$ and $\text{Cov}(\text{C}_3\text{H}_x^+, \text{S}^{4+}/\text{O}^{2+})$, respectively. The noise in these covariance maps is comparable to the relevant signature. This is due to the very few S^{n+} that are recorded. Panel f) shows the analogous integral to Panel e) and shows a preference to recoil in opposite directions. No measurable covariance was observed between multiply charged sulfur ions and other possible fragments, such as $\text{C}_4\text{H}_4\text{O}^+$ or C_2H_x^+ .

Figure 7.16 shows the recoil-frame angular covariance analysis for the CSH^+ ion and X ions, where X is defined as an ion in the m/z range (25-29), corresponding to C_2H_x^+ , CH_xO^+ , and $\text{C}_3\text{H}_x\text{O}^{2+}$ ions. These ion correlations were identified through ToF covariance analysis and assigned through complementary PIPICO analysis. The PImMS dataset cannot resolve these separate ions by ToF and therefore the covariance maps (left and central panels) show the sum of all the contributing covariances. In $\text{Cov}(\text{X}, \text{CSH}_x^+)$ (left), at least two distinct covariance signatures are

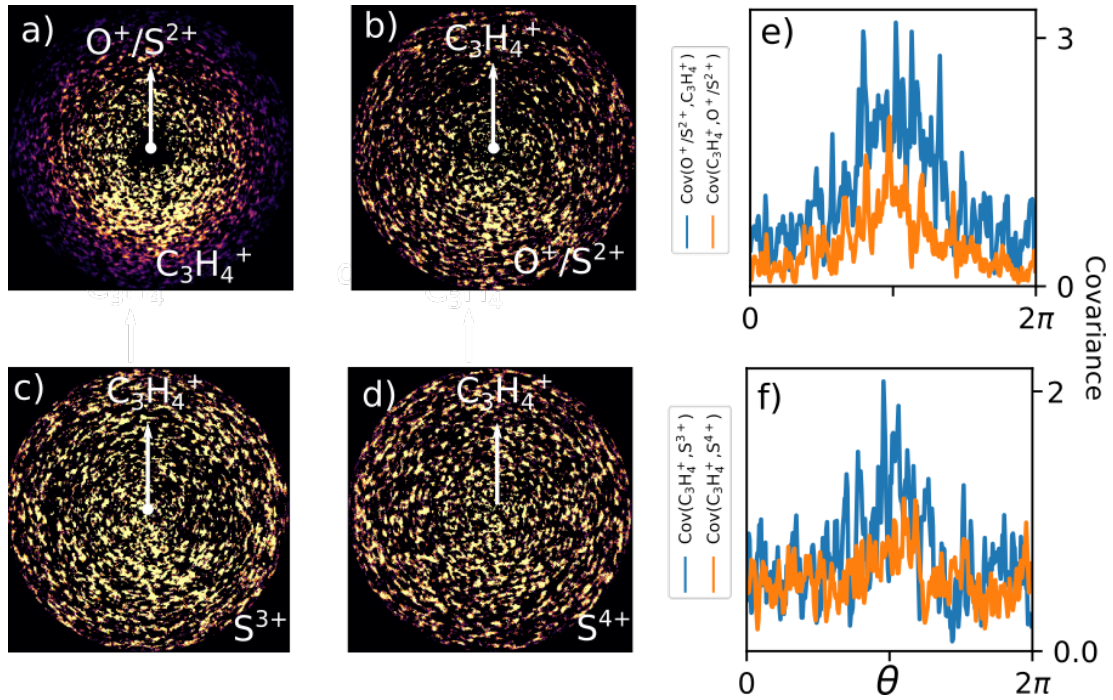


Figure 7.15: Recoil-frame angular covariance maps, $Cov(C_3H_4^+, S^{n+})$. Panels a) and b) show $Covs(C_3H_x^+, S^{2+}/O^+)$. Panels c) and d) show $Cov(C_3H_x^+, S^{3+})$ and $Cov(C_3H_x^+, S^{4+})$. Panels e) and f) show the radial integration of each of the covariance maps.

observed. One broad signature at lower radii and a narrower covariance signature at higher radii. From the coincidence experiments taken with a photon energy of 180 eV, four ion correlations were observed (Section 7.4.3). Qualitatively, it would be expected that the two-body break-ups involving CSH_x^+ and $C_3H_xO^{2+}$ ions would result in a higher velocity and a more restricted angular distribution and the broad feature would be a result of the break-up with CH_xO^+ . Similarly, in $Cov(CSH_x^+, X)$, the feature at smaller radii would correspond to the two-body three-charge break-up. Panel (c) shows the partial radial-radial covariance between these ions. The partial covariance map is quite noisy, however, there are two distinct covariance signatures at different radial pairs.

The first radial correlation is marked by the ellipse centred around (50, 80) and appears at a CSH_x^+ radius of ≈ 80 pixels and at a radius of ≈ 50 pixels in X. These are not exactly momentum-matched, however, the most intense part of the covariance signal is obscured by the noise. This does correspond to the higher radius and BTB feature in CSH_x^+ , which was qualitatively expected for

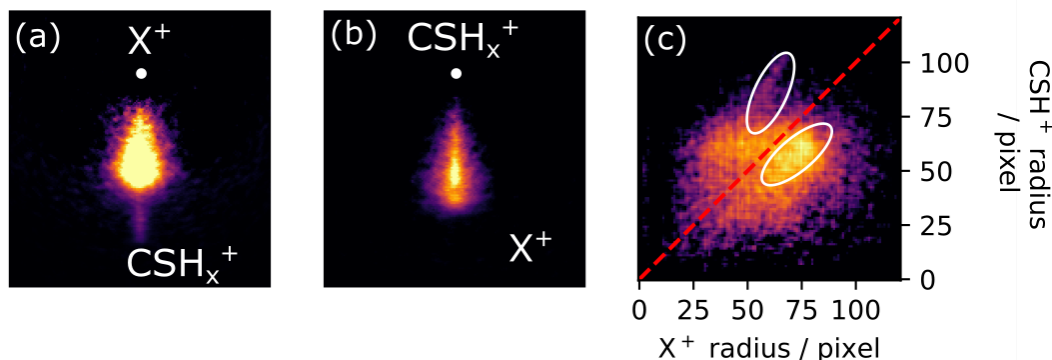


Figure 7.16: Panels (a) and (b) show the recoil-frame angular covariance maps, $Cov(X, CSH_x^+)$ and $Cov(CSH_x^+, X)$, respectively, where X is an ion within the mass-to-charge range, $25 < m/z < 29$. Panel (c) shows the radial-radial covariance between the two mass-to-charge fragments, showing two ion correlations.

this Coulomb explosion pathway.

The second correlation is marked by the ellipse centred around (75, 55) and appears at a CSH_x^+ radius of ≈ 55 pixels and at a radius of ≈ 75 pixels in X . This corresponds to $X = CH_xO^+$ which was also observed in the PIPICO data. Again, the lighter ion, CH_xO^+ , has the larger velocity and this corresponds to the broader covariance signal. Through radial-radial covariance mapping, the many correlations observed in the recoil-frame angular covariance map can be directly attributed to specific ion pairs.

7.4.5 Delay-dependent Covariance

This section will investigate any delay-dependence in the angular covariance maps outlined in the previous Section. Static delay scans were undertaken to obtain high statistic data over a range of pump-probe delays in order to achieve high quality covariance maps as the reaction evolves. Data were recorded over a pump-probe delay range of $t_0 \pm 3$ ps.

Figure 7.17 shows the delay-dependent yield of low KER S^{3+} and S^{4+} ions for this dataset. Similar plots have been discussed previously in the Chapter and are a good indicator of temporal overlap, t_0 . The channel yield should show an exponential increase as the pump-probe delay moves through t_0 . The channel yield

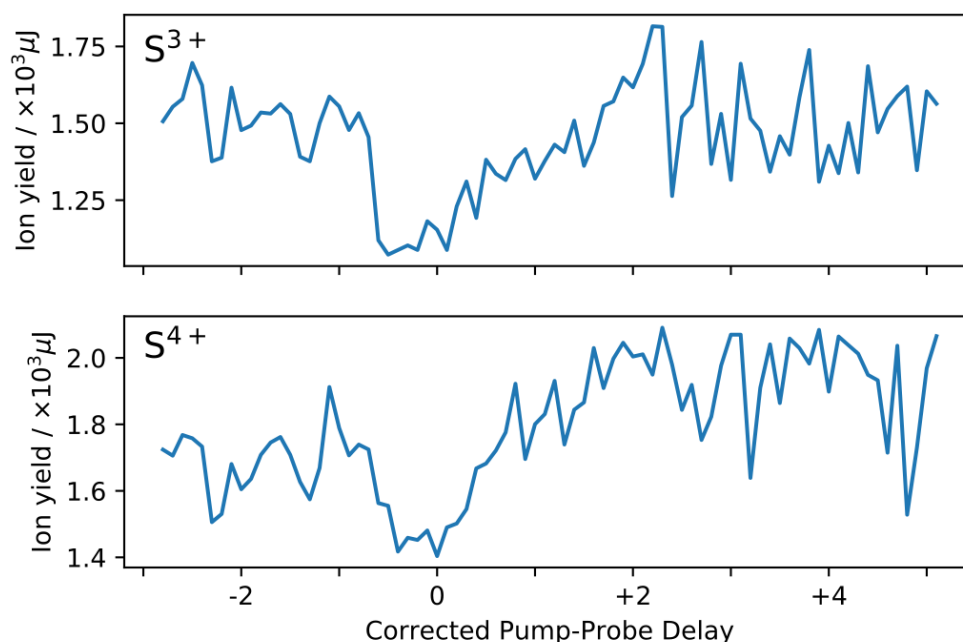


Figure 7.17: Delay-dependent yield of low KER S^{3+} and S^{4+} ions. The ion yield should appear as an exponential rise with increasing pump-probe delay. An artefact in the data results in an unexpected yield increase. As the cause cannot be accounted for, the data cannot be reliably used for delay-dependent data analysis.

behaves as expected for the delay range 0 – 4 ps, however at UV late delays, there is a large increase in yield in both ions which has no photochemical basis.

The cause for this anomalous result could be a result of experimental drift. Experimental drift could cause the delay stage to deviate significantly over the course of acquiring data or periods of elevated pulse energies. However, as static delay scans were performed systematically by taking one round of measurements and repeating after completion, it is unlikely that experimental drift could account for the large discrepancies. Unfortunately, these artefacts render the associated laser shots unsuitable for studying delay-dependent covariances. Instead, the data around t_0 and at UV early delays has been considered. For comparison, FEL only data has been used which comprises only 65,000 shots which makes a fair comparison difficult. This also precludes a detailed comparison of UV early and late ToF covariance.

Figure 7.18 shows the delay-dependent angular covariance maps for the CH_xO^+ and $C_3H_xS^+$, and CSH_x^+ and $C_3H_xO^+$ ion pairs. The first two rows show the

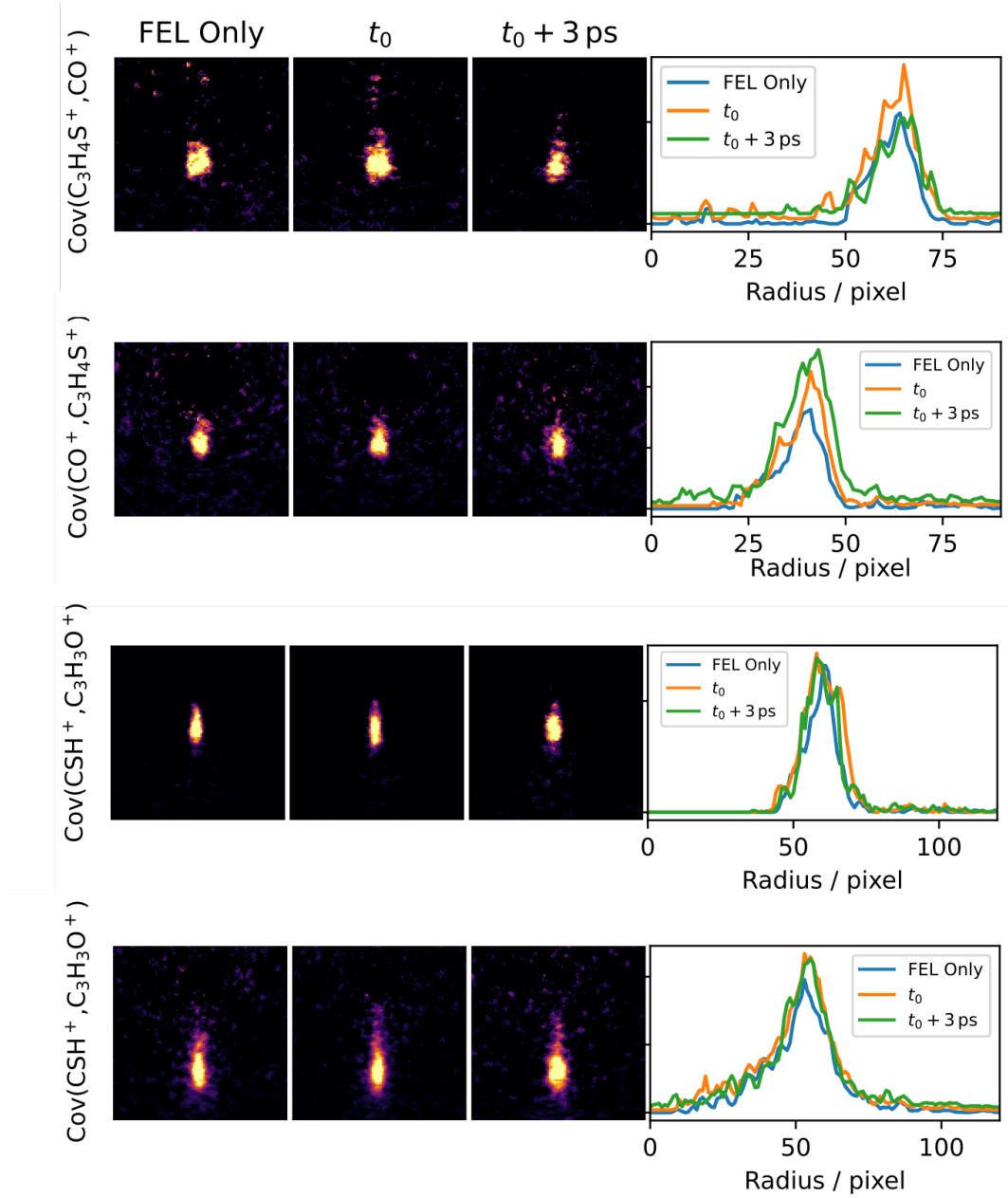


Figure 7.18: Delay-dependent angular covariance maps for the CH_xO^+ and $\text{C}_3\text{H}_x\text{S}^+$, and CSH^+ and $\text{C}_3\text{H}_x\text{O}^+$ ion pairs. First three columns: FEL only, $\approx t_0$, UV Early. Right column: velocity projection comparison of each covariance map.

covariance maps $\text{Cov}(\text{C}_3\text{H}_x\text{S}^+, \text{CH}_x\text{O}^+)$ and $\text{Cov}(\text{CH}_x\text{O}^+, \text{C}_3\text{H}_x\text{S}^+)$, calculated for FEL only data, at around t_0 , and UV early data. Both display a strong back-to-back covariance signal as before. The final column shows the velocity projection of each covariance map. In the previous Chapter investigating the UV-IR photoexcitation, there was some evidence of a UV-dependent covariance signal in this ion pair at a lower velocity, consistent with a newly formed photoproduct. In the UV-XUV data, there does not appear to be conclusive evidence of a pump-probe dependent covariance feature. In $\text{Cov}(\text{CH}_x\text{O}^+, \text{C}_3\text{H}_x\text{S}^+)$, there is a small shoulder that appears in the UV-early data that is not present in the FEL only.

The last two rows show $\text{Cov}(\text{CSH}_x^+, \text{C}_3\text{H}_x\text{O}^+)$ and $\text{Cov}(\text{C}_3\text{H}_x\text{O}^+, \text{CSH}_x^+)$, respectively. The covariance maps (first three columns) appear similar and each display a strong back-to-back covariance signal. The velocity projections of these covariance maps (final column) do not show any changes. This was repeated for each ion pair discussed in the previous Section.

7.4.6 Discussion

A number of fragmentation pathways of thiophenone have been observed through ToF covariance. These ion correlations are in good agreement with probe only coincidence data performed at ALS. These ion correlations were further investigated through recoil-frame angular covariance using the corresponding PImMS images and the ion momenta were found to be strongly back-to-back two body breakups or broadly back-to-back break-ups. There have been no clear signs of delay-dependence through angular covariance analysis. There is a suggestion of a UV- dependent covariance signal in $\text{Cov}(\text{CH}_x\text{O}^+, \text{C}_3\text{H}_x\text{S}^+)$, akin to that observed in Chapter 6. However, the lack of delay-dependence in other ion pairs indicates that there is not enough evidence to support the signature. The unaccounted artefact in the static delay data resulted in much of the dataset inappropriate for delay-dependent analysis. This data would likely have made a positive impact on the quality of the covariance analysis and probably have allowed a more decisive conclusion to be made.

7.5 Conclusion

In this Chapter, the UV photoexcitation of thiophenone at 267 nm has been investigated *via* XUV probe at 6.3 nm (197 eV). The UV photoexcitation has been studied at two UV pulse energies. At high UV intensities ($I = 2 \times 10^{12} \text{ W cm}^{-2}$), multiphoton UV absorption processes dominated. This was observed in the fragmentation of thiophenone, the sharp loss of high kinetic energy ions after t_0 , and the appearance of ‘Coulomb’ curves in multiple charged sulfur ions. At low UV intensities ($I = 1 \times 10^{11} \text{ W cm}^{-2}$), some multiphoton absorption dynamics were observed but reduced dramatically. Some velocity-dependent channels showed slight enhancements.

Through high-resolution ToF partial covariance analysis, many ion correlations were observed following the XUV ionisation of thiophenone. Angular correlations between these ion momenta were established through recoil-frame angular covariance using the corresponding PImMS dataset. Both two-body and three-body break-ups were observed through this analysis. Inconclusive ion correlations from the ToF analysis were identified from PIPICO data on thiophenone performed at the ALS facility.

Delay-dependent angular covariance analysis did not yield any significant information on the photoexcitation dynamics. The main cause of this was the lack of statistics that could be used as a result of an unexplained artefact. A majority of the laser shots during the high statistic static delay scans were affected. Ultimately, more statistics are necessary to make reliable conclusions from the data.

7.5.1 Future Experiments

This section will discuss the success of studying the gas-phase ring-opening of heterocyclic molecules such as thiophenone and outline any modifications that may help to assert unambiguous isomerisation. As discussed in the previous section (and in the previous Chapter), indications of ring-opening have been observed through various covariance techniques. However, there has not been a categorical signature that unambiguously identifies a ring-opening process.

As a result of the work in this Chapter, future investigations on this system or similar systems will have a clearer idea of signatures to look for and the methodology to achieve these signatures. The key to successful covariance analysis is through the aggregation of enough statistics (*i.e.* laser shots) at photochemically relevant pump-probe laser delays. The critical measurement to be sure of is the temporal overlap, t_0 , of the two lasers. By using the rise in the yield of the low kinetic energy of S^{n+} ions, this value can be identified. Once t_0 is established, the accumulation of data can occur. Repeated delay scans from 1 ps late to 3 ps early with a maximum delay step of 100 fs would be sufficient to capture the dynamics with enough statistics. It would also be pertinent to perform some experiments at long delays ($t_0 + 10$ ps) to capture the long time dynamics[18] such as CO elimination and ring-closing mechanisms. During the accumulation of delay scans, the yield of low KER S^{n+} ions should be checked regularly to ensure that no unexpected drift or laser output effects the dynamics. A high level of statistics for FEL only data should be taken to reliably understand the probe only effects.

It could also be advantageous to investigate the thiophenyl derivative, 1-bromothiophene. This molecule has some benefits to thiophenone. Firstly, the mass-to-charge degeneracy present in thiophenone is immediately removed which will improve the assigning of velocity features in ion images. This would encounter some problems in itself with overlapping mass-to-charge fragments such as Br^{2+} and $C_3H_x^+$, and Br^{3+} and $C_2H_x^+$. However, these would not be an issue for covariance analysis as a Br^+ could not be in covariance with Br^{2+} .

Bromine has a large XUV absorption cross-sections and would therefore be a very convenient atom to target for inner-shell ionisation. At a photon energy of around 200 eV, as was used in these experiments, the absorption cross-section of the $Br(3d)$ orbital is comparable to the $S(2p)$ orbital and typically both these atoms would be ionised[113]. This pair of ions would allow for convenient markers to track the structural dynamics of the photoexcitation through covariance analysis.

The UV dissociation of bromine[56, 233, 260] would becoming a competing pathway, however, the advantages of having the two marker ions for covariance

analysis would far outweigh a depletion in the ring-opening channel. Further, the covariance signal of the bromine dissociation would be very different to that of the ring-opening signature.

8

Strong-Field Ionisation Dynamics of OCS

8.1 Introduction

This Chapter will investigate the Coulomb explosion dynamics of carbonyl sulfide, OCS, following strong-field ionisation at 800 nm at varying pulse energies. Given the simple structure of OCS, it was deemed a model first system to investigate Coulomb explosion dynamics in a Coulomb explosion imaging experiment using FLO. This would allow for an intuitive interpretation of covariance analyses and thus gain an understanding of the Coulomb explosion pathways that can occur for a simple molecule before advancing to more complex systems. At different pulse energies, the initial charge state of target molecules varies resulting in different Coulomb explosion pathways and branching ratios. Velocity-mapping in conjunction with various covariance techniques will allow for these pathways to be disambiguated and reveal the dynamics of the Coulomb explosion.

8.2 Experimental Methods

The Coulomb explosion dynamics of OCS was investigated by Coulomb explosion imaging, with an intense non-resonant 800 nm probe pulse (35 fs). The laser pulse is crossed perpendicularly with a molecular beam of OCS (5% mix in Helium). Pulse energies were controlled *via* beam splitters and a variable attenuator, see

Chapter 2 for more details. Resultant ions are velocity mapped in DC-slicing ion optic configuration onto a two-dimensional position sensitive detector.

As the laser intensity is increased, ion signal increases non-linearly. In order to reduce strain on the detector and offset PImMS saturation effects, the ion signal was reduced by decreasing the backing pressure of the OCS mixture and optimising the timing of the molecular beam such that its intersection with the laser pulse occurred at the coldest part of the beam.

8.3 Coulomb Explosion Dynamics at Low Intensity

8.3.1 Time-of-Flight Analysis

Figure 8.1 shows the mass spectrum for OCS following Coulomb explosion with a pulse energy of $100\mu\text{J}$ as recorded by a PImMS2 camera. The mass spectrum has been obtained from the centroided time-of-flight spectrum and calibrated for mass-to-charge.

A number of atomic and fragment ions are produced and the corresponding mass peaks are labelled in Figure 8.1. The dominant ions produced are S^+ and CO^+ with an appreciable production of molecular CS^+ and CO^{2+} and atomic C^+ and O^+ ions. Some parent cation and dication are also observed. It should be noted that the yields of these ions are underestimated as a result of saturation of PImMS pixels, particularly a result of a high number of background ions (such as H_2O^+). This was previously mentioned in Chapter 7. The result of this is that VMI images of higher mass-to-charge ratio ions often appear to have a hole at the centre of the image.

The charges of ions observed in the mass spectrum suggest that at a pulse energy of $\sim 100\mu\text{J}$, the parent molecule is typically fragmented into ions with one or two charges.

The next section will investigate the VMI ion images of recorded by the PImMS camera and associate with these channels.

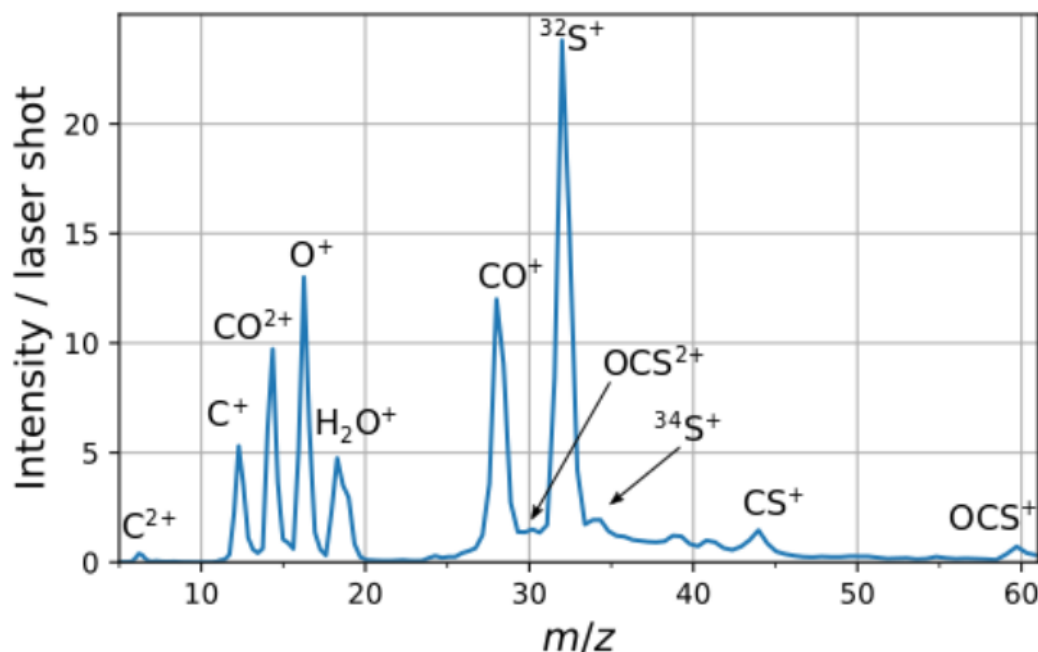


Figure 8.1: Mass spectrum of OCS upon strong-field ionisation at 800 nm with a pulse energy of $\sim 100\mu\text{J}$. Ion peaks are labelled. See text for more details.

8.3.2 VMI Images

The VMI ion images for the major peaks in the mass spectrum in Figure 8.1 are shown in Figure 8.2. The left column shows the VMI images for the S^+ , CO^+ , CS^+ , O^+ and S^{2+} , and CO^{2+} , respectively. The left half of the image shows the crushed image recorded for each ion and the right half shows the inverted image using the pBASEX algorithm[129]. The central and right columns show the corresponding velocity and kinetic energy release (KER) distributions of the inverted images, respectively.

Firstly, it is apparent from the VMI images that generally there is an appreciable amount of intensity toward the centre of the image. This corresponds to ions with a comparably low KER and not borne from a Coulomb explosion. Such ions are likely formed *via* dissociative ionisation whereby the strong-field removes one or two electrons from the parent molecule which simply dissociates into a charged species and a neutral cofragment. This dissociative ionisation channel is particularly prominent for the S^+ , CO^+ , CS^+ , and CO^{2+} ions.

Secondly, it is notable that all the velocity features (including the dissociative ionisation channels) exhibit an up-down anisotropy. The ionisation of molecules in

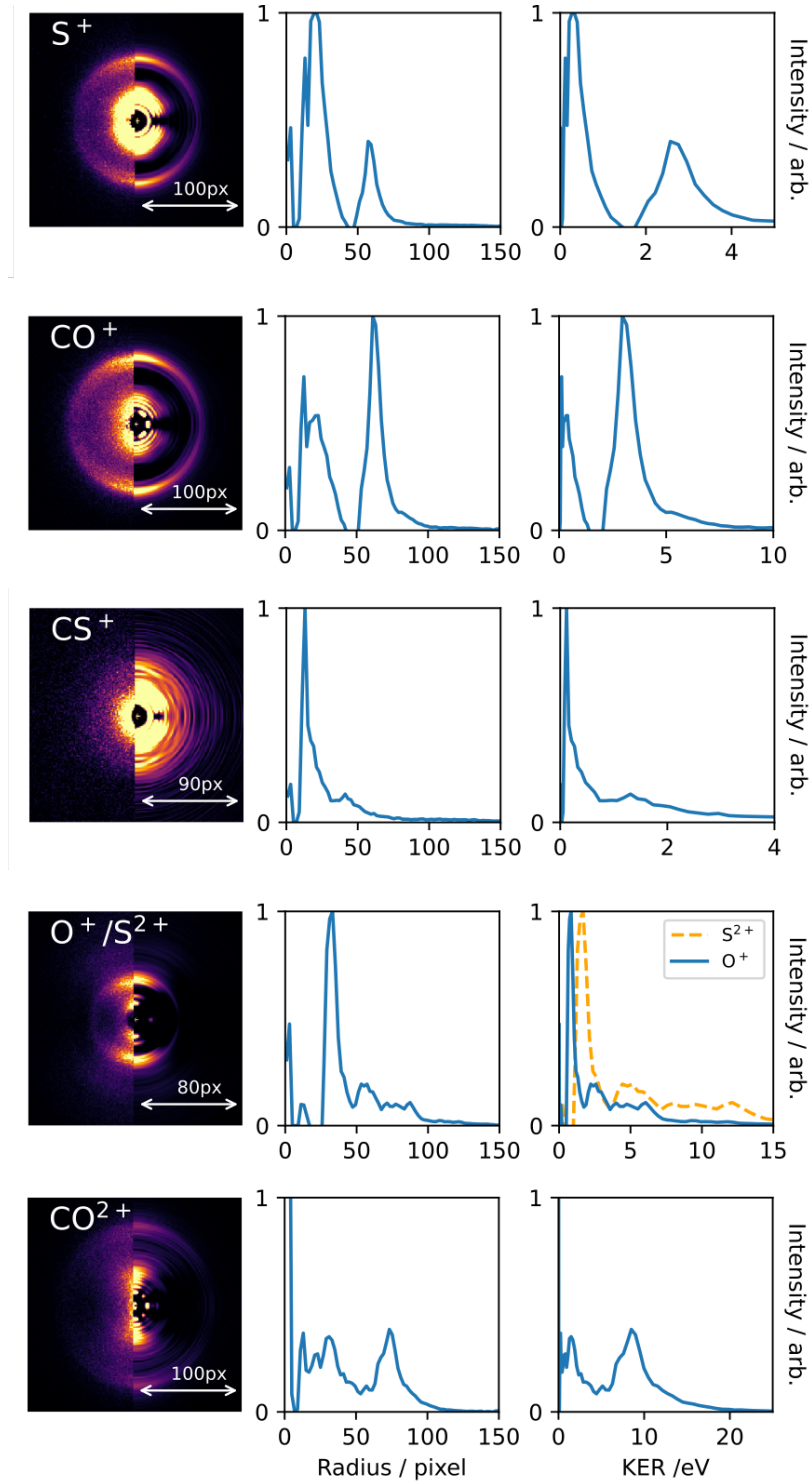


Figure 8.2: First column shows VMI ion images of the predominant ions produced in the mass spectrum in Figure 8.1 following strong-field ionisation of OCS. The left half of the image shows the crushed image recorded for each ion and the right half shows the inverted image using the pBASEX algorithm[129]. Second column shows the corresponding velocity distribution of each ion image. The third column shows the corresponding kinetic energy release (KER) distribution of each ion image.

a strong-field is more preferential when molecules align with the electric field polarisation[228, 261].

Additionally to the dissociative ionisation channel, the sulfur ion has a sharp velocity feature at around 60 pixels or 2.9 eV and does not appear to have any other channels. The carbonyl ion has a strong feature at around 60 pixels or 2.8 eV and some weaker contributions at higher velocities. The CS^+ fragment has a velocity feature at around 45 pixels (1.7 eV).

The O^+ and S^{2+} ions have a degenerate mass-to-charge ratio and as a result their shared velocity distribution is rich in features. At least three distinct high velocity features are present in addition to the intense dissociative ionisation channel. The corresponding KER distributions are different for each ion as the KER is related to the velocity and charge of an ion.

The CO^{2+} ion has a very strong dissociative ionisation channel and a weak channel at higher velocities. There appears to be structure the dissociative ionisation channels of in the inverted image, however, these are unlikely to be real and an artefact of a poorly inverted image.

The next section will explore these Coulomb explosion dynamics through recoil-frame angular covariance analysis.

8.3.3 Coulomb Explosion Dynamics

This section will discuss the recoil-frame angular covariance analysis to attempt to determine ion momenta correlations. Each section will discuss a Coulomb explosion pathway.

$\text{CO}^+ + \text{S}^+$

Figure 8.3 displays the recoil-frame angular covariance analysis for the CO^+ and S^+ ion pair. Panels 8.3 a) and 8.3 b) show the raw and inverted images for the CO^+ and S^+ ions. Panels 8.3 c) and 8.3 d) show the covariance maps, $\text{Cov}(\text{S}^+, \text{CO}^+)$ and $\text{Cov}(\text{CO}^+, \text{S}^+)$, respectively where the reference ions are directed toward the top of the page. Both covariance maps display a strong covariance signal at around

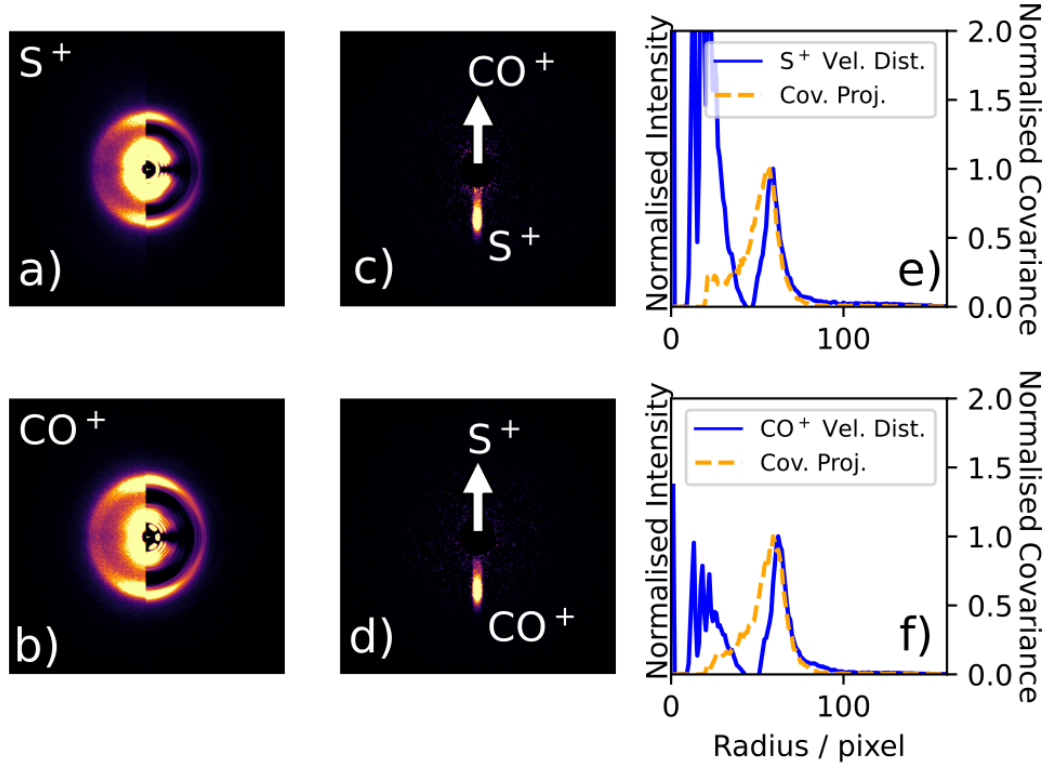


Figure 8.3: Panels a) and b) show the raw and inverted ion images for CO^+ and S^+ . Panels c) and d) show the covariance maps $\text{Cov}(\text{CO}^+, \text{S}^+)$ and $\text{Cov}(\text{S}^+, \text{CO}^+)$. Panels e) and f) show the velocity projection of the covariance maps in comparison to the velocity distribution of the plotted ion. The velocity projection of the Coulomb explosion channel between CO^+ and S^+ is aligned with the main peak in the respective velocity distributions.

60 pixels, at a recoil angle of 180° . This is evidence that the following Coulomb explosion pathway is present and a dominant (CE) channel at these pulse energies.



Panels 8.3e) and 8.3f) show the velocity distribution of the CO^+ and S^+ ions (blue) in comparison with the velocity projection of the recoil-frame angular covariance maps (orange). The covariance projections align exactly with the corresponding velocity distributions. The covariance projection is broader than the peak of the velocity distribution of the inverted image, tailing to lower velocities. This is because the covariance projection includes ion correlations out of the

plane of the detector which are measured at lower radii by PImMS. This will be discussed in greater detail later.

$\text{CS}^+ + \text{O}^+$

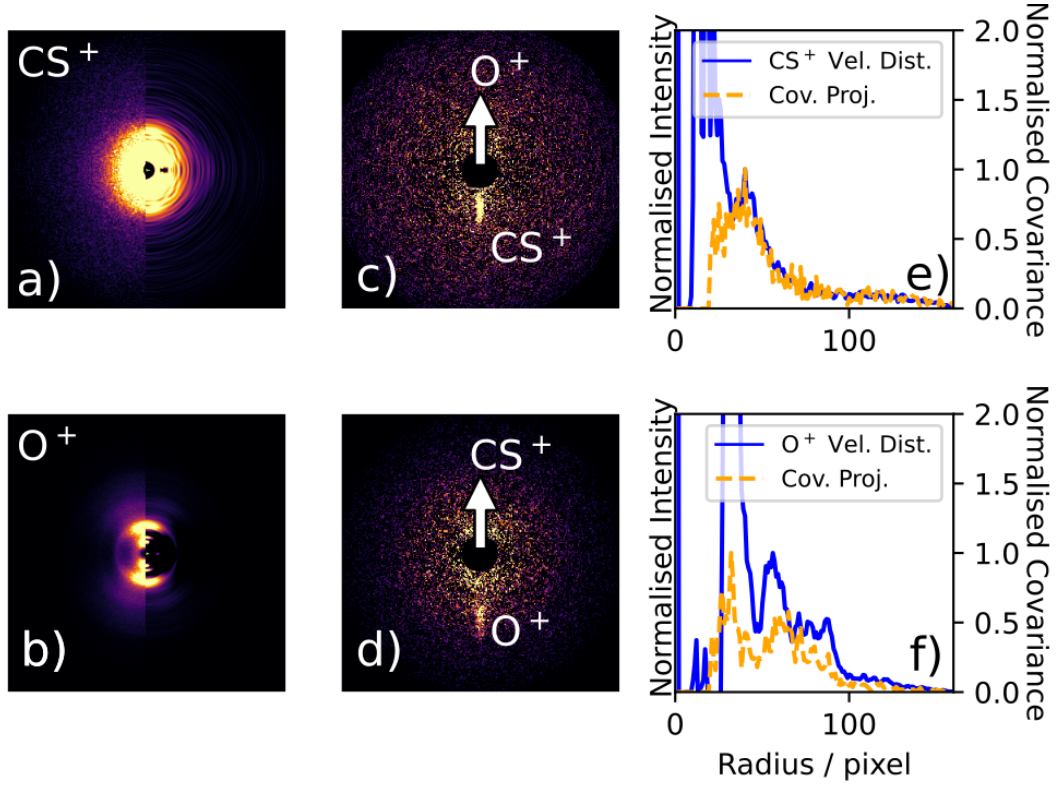


Figure 8.4: Panels a) and b) show the raw and Abel inverted ion images for CS^+ and O^+ . Panels c) and d) show the covariance maps $\text{Cov}(\text{O}^+, \text{CS}^+)$ and $\text{Cov}(\text{CS}^+, \text{O}^+)$. Panels e) and f) show the velocity projection of the covariance maps in comparison to the velocity distribution of the plotted ion. The velocity projection of the Coulomb explosion channel between CS^+ and O^+ is aligned with the main peak in the respective velocity distributions.

Figure 8.4 shows the equivalent recoil-frame angular covariance analysis for the CS^+ and O^+ ion pair. Figure Panels 8.4 a) and 8.4 b) show the raw and Abel inverted images for the CS^+ and O^+ ions, respectively.

Figure Panels 8.4 c) and 8.4 d) show $\text{Cov}(\text{O}^+, \text{CS}^+)$ and $\text{Cov}(\text{CS}^+, \text{O}^+)$, respectively. Both display a strong covariance signal at a recoil angle of 180° to the respective reference ions. The projection of these covariance signals is compared to the velocity distribution of the plotted ions in Figure Panels 8.4 e) and 8.4 f). The projection of $\text{Cov}(\text{O}^+, \text{CS}^+)$ aligns with the velocity peak in the

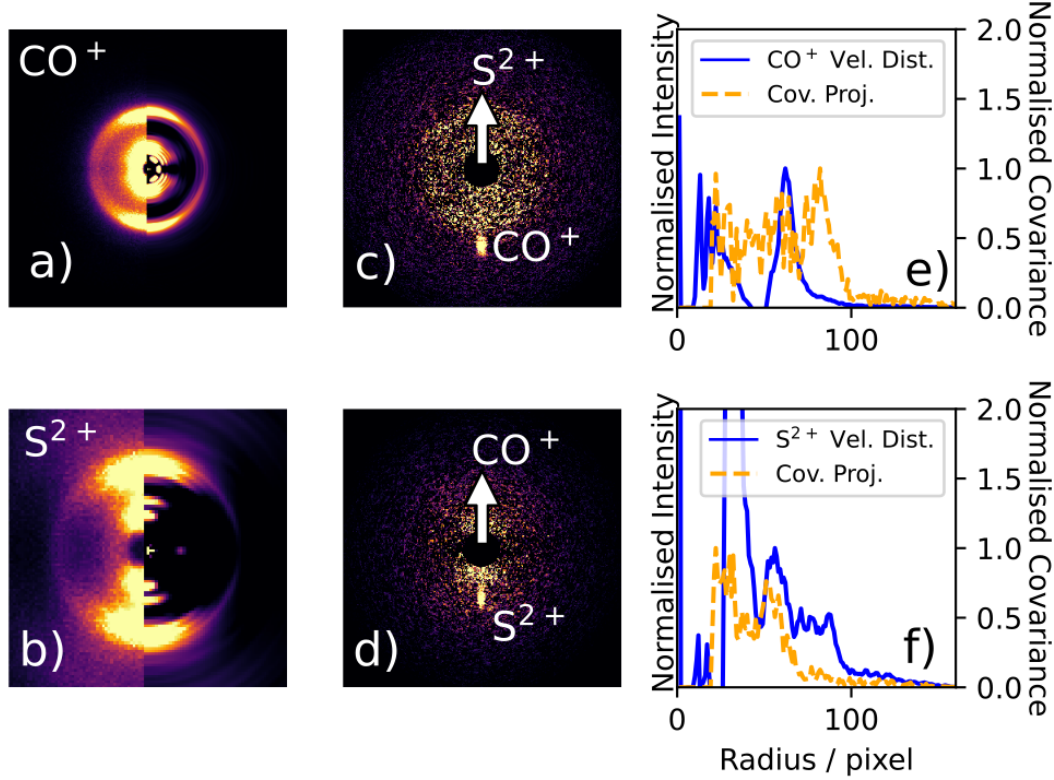


Figure 8.5: Panels a) and b) show the raw and inverted ion images for CO^+ and S^{2+} , respectively. Panels c) and d) show the recoil-frame angular covariance maps, $\text{Cov}(\text{S}^{2+}, \text{CO}^+)$ and $\text{Cov}(\text{CO}^+, \text{S}^{2+})$, respectively. Panels e) and f) show a comparison of the velocity projections of the covariance maps with the Abel inverted velocity distributions of the ion images.

CS^+ velocity distribution at ~ 43 pixels. The equivalent projection of $\text{Cov}(\text{CS}^+, \text{O}^+)$ aligns less clearly with a peak in the O^+ velocity distribution. However, the calculated momentum-matched velocity peak for the O^+ for this channel (using $r(\text{CS}^+) = 43$ pixels) is 71 pixels, which does align with a peak in the velocity distribution. These show that this Coulomb explosion channel is present.

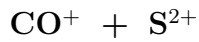


Figure 8.5 shows the equivalent recoil-frame angular covariance analysis for the S^{2+} and CO^+ ion pair. Figure Panels 8.5 a) and 8.5 b) show the raw and inverted images for the CO^+ and S^{2+} ions, respectively.

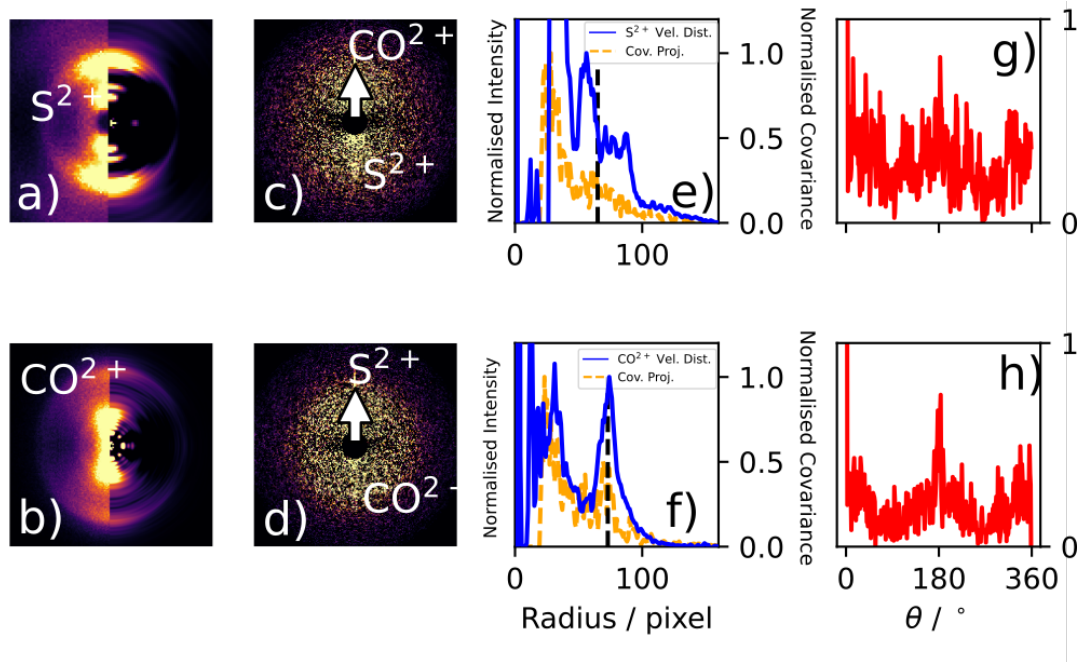


Figure 8.6: 180° is observed indicating that this ion correlation is real. The strong covariance observed at 0° is a result of contamination of the ToF peaks which partially overlap. See text for more details.

Figure Panels 8.5 c) and 8.5 d) also show a strong covariance signal at a recoil angle of 180° to the respective reference ions. This is indicative of a two-body Coulomb explosion channel. This channel indicates that the parent molecule gains at least three charges *via* strong-field ionisation at these pulse energies.



From Figure Panel 8.5 e), the velocity projection of the covariance map aligns with the most intense peak in the O^+/S^{2+} velocity distribution at around ~ 55 pixels. The momentum-matched velocity feature in the CO^+ velocity distribution is at around 83 pixels and constitutes a minor channel at higher radii to Channel (8.1). This demonstrates that Channel (8.1) is by far the dominant channel for the CO^+ ion.

8.3.3.1



8.6 a) and 8.6 b) show the raw and inverted ion images for the CO^{2+} and S^{2+} ion pair. Figure Panels 8.6 c) and 8.6 d) show the recoil-frame covariance maps,

$\text{Cov}(\text{CO}^{2+}, \text{S}^{2+})$ and $\text{Cov}(\text{S}^{2+}, \text{CO}^{2+})$, respectively. The covariance maps are noisy and do not show an obvious covariance signal as in previous ion pairs. However, there is a small covariance signal at 180° to the reference ions. Figure Panels 8.6 e) and 8.6 f) compare the velocity projections of the covariance maps to the ion velocity distributions. Panel 8.6 e) shows a clear agreement between the two velocity peaks at 73 pixels. The comparison is less clear in the S^{2+} velocity distribution on account of the multiple features that contribute to the ensemble distribution. The peak velocity of the S^{2+} momentum-matched to the CO^{2+} peak (of 73 pixels) corresponds to 67 pixels. These velocities are drawn as dashed lines in the respective panels to illustrate their positions in the velocity distribution. The peak at 67 pixels in the S^{2+} velocity distribution corresponds to a shoulder at higher velocity to the $\text{S}^{2+}/\text{CO}^+$ channel. This is expected as the Coulomb energy is proportional to the total charge. Figure Panels 8.6 g) and 8.6 h) show the radial integration of the covariance map over the radii of the signatures. There is a clear peak at 180° in both covariance maps which suggests that although weak, these are real covariance signals. The intensity enhancement at around 0° and 360° is a result of auto-covariance between ions that overlap in the ToF spectrum. CO^{2+} and S^{2+} partially overlap in the ToF spectrum and as a result, the ion signal appears in covariance with itself.

$\text{S}^{2+} + \text{O}^+$

Figure 8.7 shows the the recoil-frame angular covariance map for the S^{2+} and O^+ ion pair. Panel a) shows the raw and inverted ion image for the S^{2+} and O^+ ions. Panel b) shows the recoil-frame angular covariance map for the ion pair. Here, there is a single covariance map as a result of the mass-to-charge degeneracy. As a consequence there is an inevitable strong auto-covariance observed along the recoil-frame vector. However, there is some covariance directed 180° to the reference ions and these derive from the following Coulomb explosion.



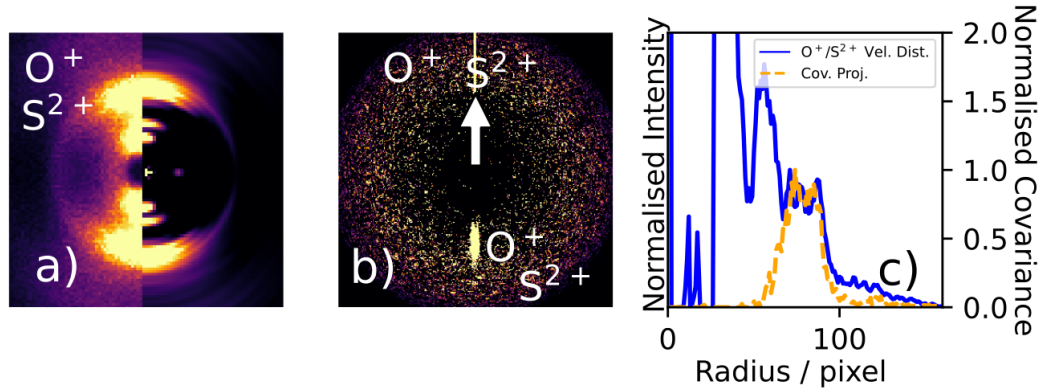


Figure 8.7: Recoil-frame covariance analysis for the O^+ and S^{2+} ion pair. Panel a) shows the raw and inverted S^{2+} and O^+ ion image. Panel b) shows the recoil-frame angular covariance map. Panel c) shows the velocity projections of the covariance map in comparison to the ion velocity distribution.

This is not a pure two-body break-up as the carbon is not observed, however as the ions lie linearly the momentum that the carbon carries away does not cause the ion trajectories to deviate greatly from the back-to-back recoil.

Two distinct peaks are resolved in the velocity projection of the covariance map. These are shown in Panel b) and overlap well with the two velocity peaks at around 76 pixels and 86 pixels.

Figure 8.8 shows the velocity distributions of the CO^+ ion (Panel A) and the O^+/S^{2+} ions (Panel B). The Coulomb explosion channels that have been shown through recoil-frame covariance are labelled on each velocity distribution.

The CO^+ velocity distribution, deriving from Coulomb explosion pathways, can now be fully described through covariance analysis as contributions from Coulomb explosions with S^+ and S^{2+} cofragment ions. The low velocity channel is borne from dissociative ionisation whereby a parent cation is formed and the CO-S bond breaks resulting in the CO^+ ion. The ion velocity derives from conservation of momentum as the bond breaks. As only one charge is associated with this channel, covariance analysis can not yield any further information.

Panel B shows the velocity distribution of the S^{2+} and O^+ ions. Through analysis of the Coulomb explosion dynamics, five peaks can be assigned to specific Coulomb explosion pathways (between 50 and 100 pixels).

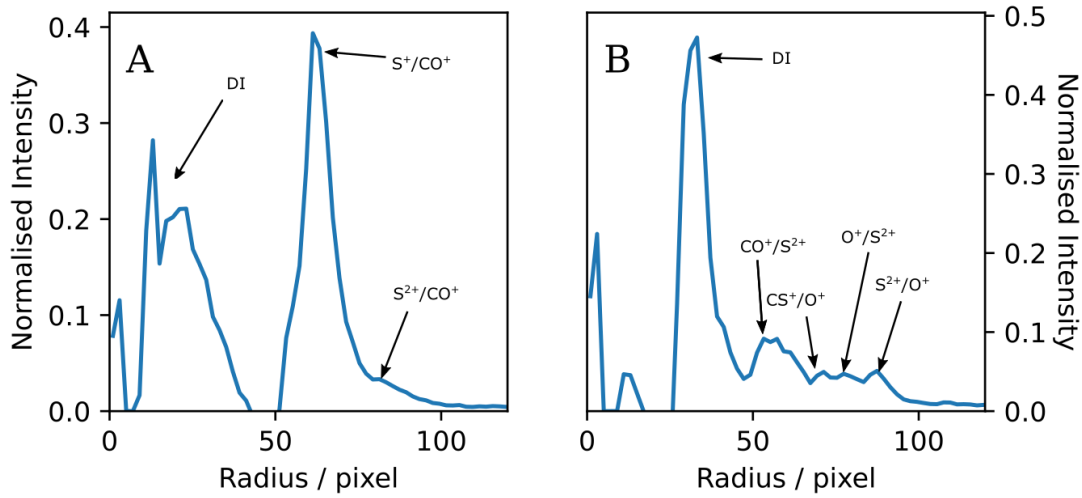


Figure 8.8: Panel A shows the velocity distribution of the CO^+ ion with each peak labelled according to the ion correlations uncovered through covariance analysis. Panel B shows the equivalent velocity distribution of the O^+ and S^{2+} ions. DI denotes the dissociative ionisation channel.

8.4 Coulomb Explosion Dynamics at Medium Intensity

This section investigates the Coulomb explosion dynamics for OCS at a pulse energy of $200 \mu\text{J}$. The data was accumulated over 43,240 laser shots.

8.4.1 Time-of-Flight Analysis

Figure 8.9 shows the mass spectrum following the Coulomb explosion of OCS at a pulse energy of $200 \mu\text{J}$. The blue trace shows the average mass spectrum and the orange trace shows a magnified mass spectrum.

This mass spectrum shows many similarities to the equivalent mass spectrum shown in Figure 8.1 obtained at $100 \mu\text{J}$, with some remarkable differences. The ion intensities of the CO^+ and S^+ are still the most prevalent ions. A significant proportion of C^+ , CO^{2+} , and O^+/S^{2+} are also still observed. There is also a marked increase in the ion intensity of the O^+/S^{2+} and C^{2+} ions. The most notable difference is the formation of higher charged ions, including CS^{2+} , S^{3+} , $\text{S}^{4+}/\text{O}^{2+}$, and CO^{4+} . This is to be expected as there are more photons in each laser pulse increasing the laser intensity. This decreases the Keldysh parameter for the system

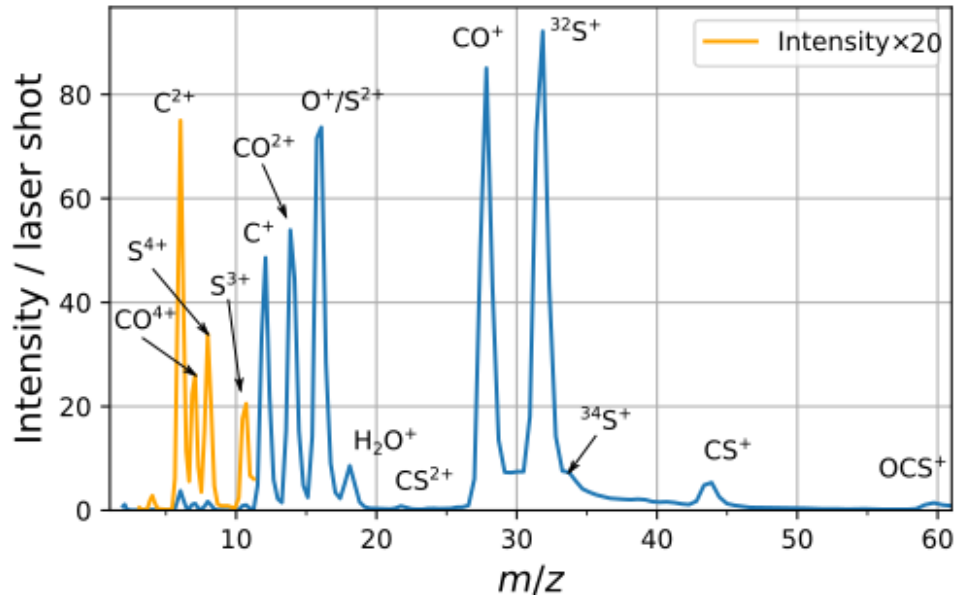


Figure 8.9: Mass spectrum for OCS after irradiation with the FLO at 800 nm with a pulse energy of $\sim 200 \mu\text{J}$. The orange trace shows a magnified mass spectrum for ions with mass-to-charge ratios, $m/z < 11$. Ions are labelled. See text for more details.

and pushes toward a more strong-field ionisation regime and more electrons are removed, increasing the number of higher charged ions produced.

8.4.2 Coulomb Explosion Dynamics

This section will investigate additional Coulomb explosion dynamics present at this pulse energy (that were not observed at lower pulse energies) through covariance analysis of different ion pairs. Naturally the number of ion correlations is increased as a result of the formation of several more charged species, each with different Coulomb explosion pathways. Each section will discuss a corresponding Figure showing the ion images, the angular covariance of an ion pair, and a comparison between the velocity projection of the covariance map and the corresponding ion velocity distribution.

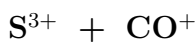


Figure 8.10 shows the recoil-frame angular covariance analysis for the CO^{+} and S^{3+} ion pair. This channel was not observed at lower pulse energies. The covariance is difficult to observe in $\text{Cov}(\text{CO}^{+}, \text{S}^{3+})$ but is clearly evident in $\text{Cov}(\text{S}^{3+}, \text{CO}^{+})$. This was observed in previous Chapters in covariance calculations where the reference

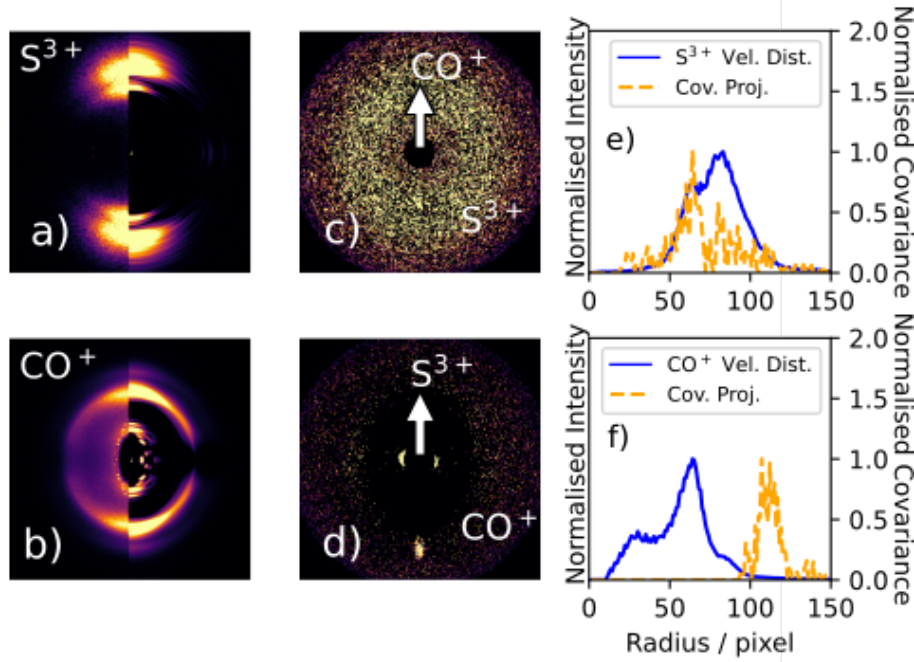


Figure 8.10: Recoil-frame covariance analysis of the CO^+ and S^{3+} ion pair. Panels a) and b) show the respective VMI images. Panels c) and d) show the recoil-frame angular covariance maps. Panels e) and f) show the velocity projections of the covariance map in comparison to the ion velocity distribution.

ion (CO^+ , here) is much more prevalent than the plotted ion (S^{3+} , see Figure 8.9 for ion yield comparisons). The velocity projections do however show a clear signal. The velocity projection of $\text{Cov}(\text{CO}^+, \text{S}^{3+})$ displays a peak at around 60 pixels that matches with the lower velocity peak in the S^{3+} velocity distribution. The complementary velocity projection of $\text{Cov}(\text{S}^{3+}, \text{CO}^+)$ indicates a peak at around 110 pixels. From investigating the CO^+ ion image and velocity distribution alone it is not clear at all that such a channel exists as it is a very minor channel. This shows the power of covariance analysis at extracting even very weak Coulomb explosion dynamics.

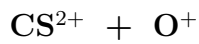


Figure 8.11 shows the the recoil-frame angular covariance analysis for the CS^{2+} and O^+ ion pair. The CS^{2+} ion was not produced at the lower laser intensity. Here, it is shown to be formed in covariance with the O^+ (akin to CS^+). There is also a substantial dissociative ionisation channel for this ion. The peak in the velocity

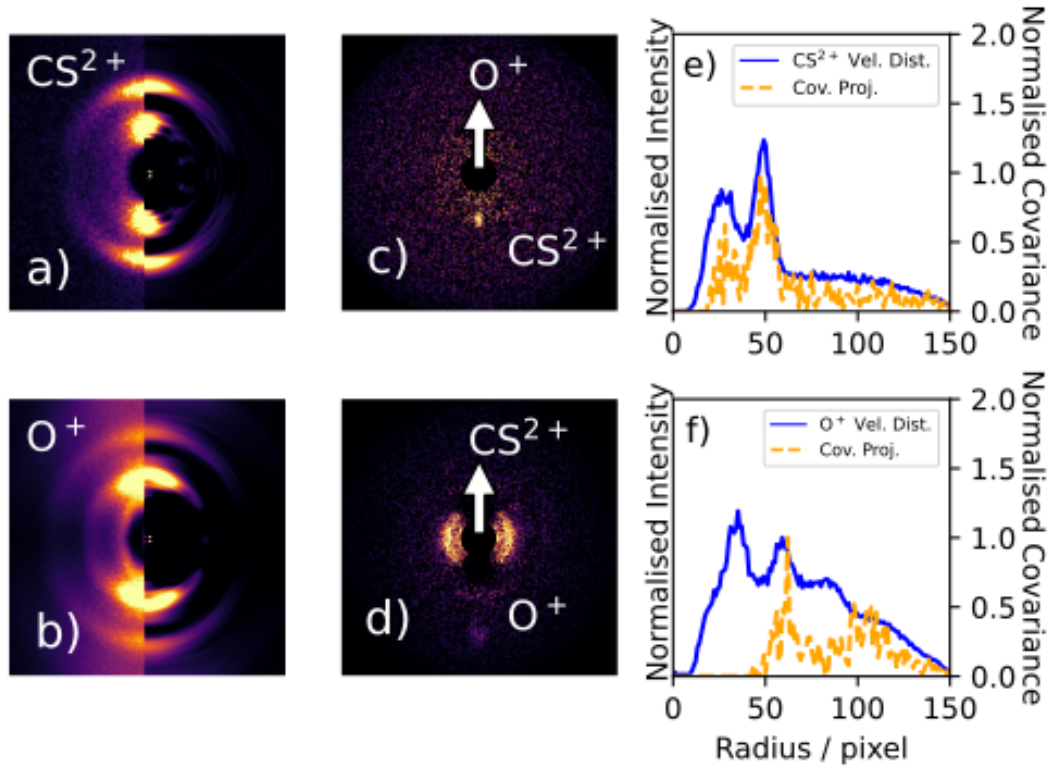


Figure 8.11: Recoil-frame covariance analysis of the CS^{2+} and O^+ ion pair. Panels a) and b) show the respective VMI images. Panels c) and d) show the recoil-frame angular covariance maps. Panels e) and f) show the velocity projections of the covariance map in comparison to the ion velocity distribution.

projection of $\text{Cov}(\text{O}^+, \text{CS}^{2+})$ aligns exactly with the CS^{2+} peak in the velocity distribution. The peak in the velocity projection of the complementary $\text{Cov}(\text{CS}^{2+}, \text{O}^+)$ is manifest as a peak at around 150 pixels. This is a result of the large mass discrepancy between the two ions and the increased charge on the two ions. In this covariance map, there is significant ‘sideways’ scattered covariance. This is false covariance, potentially related to saturation effects at low radius. It can be ruled out as a false covariance on momentum conservation grounds and as similar signatures are not observed in the reversed covariance map.

$\text{CO}^{2+} + \text{S}^{2+}$

Figure 8.12 shows the the recoil-frame angular covariance analysis for the S^{2+} and CO^{2+} ion pair. This ion pair was observed weakly at lower laser intensities, however, at these laser intensities, the Coulomb explosion pathway is more prevalent

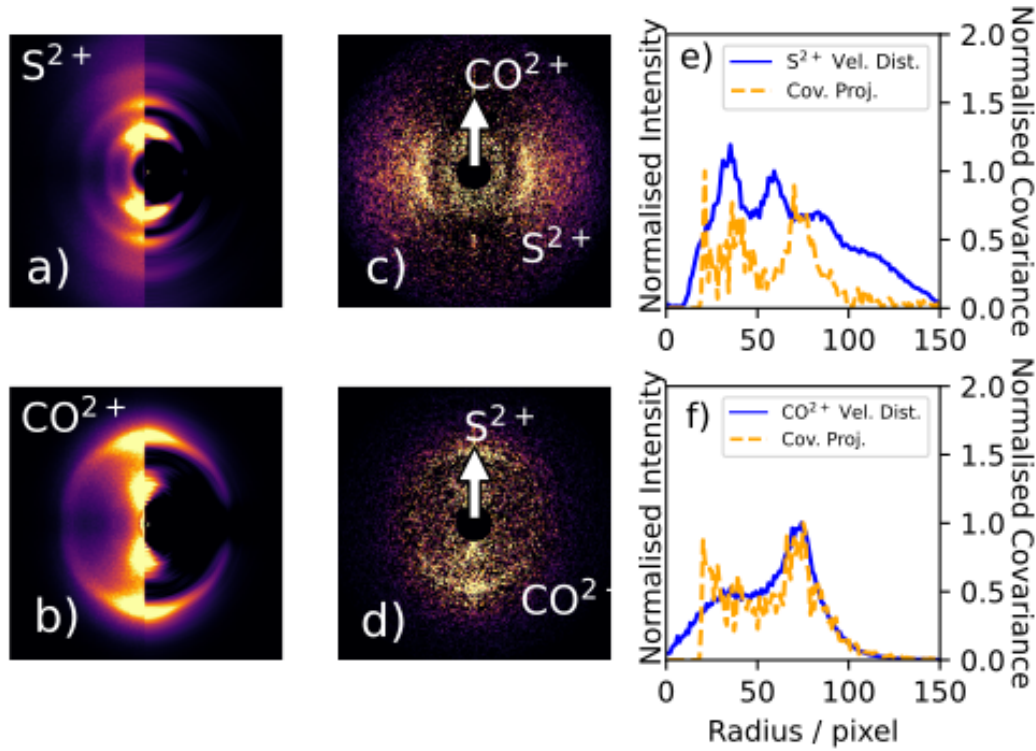


Figure 8.12: Recoil-frame covariance analysis of the CO^{2+} and S^{2+} ion pair. Panels a) and b) show the respective VMI images. Panels c) and d) show the recoil-frame angular covariance maps. Panels e) and f) show the velocity projections of the covariance map in comparison to the ion velocity distribution.

and the covariance signatures at 180° are clearly discernible. The peaks in the velocity projection of the respective covariance maps align well with peaks in the velocity distributions.

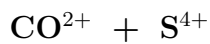


Figure 8.13 shows the the recoil-frame angular covariance analysis for the S^{4+} and CO^{2+} ion pair. This is the first ion correlation where six electrons are removed from OCS during the ionisation process. The velocity projection of $Cov(CO^{2+}, S^{4+})$ aligns with the lower velocity peak, at around 90 pixels, in the S^{4+} ion image in Panel 8.13 a). The peak in the complementary $Cov(S^{4+}, CO^{2+})$ indicates a minor peak at higher velocities to that attributed to S^{2+}/CO^{2+} . From the extracted velocity distribution of CO^{2+} , it is not clear that such a velocity feature is present. Through covariance analysis, the velocity feature can be attributed to a specific

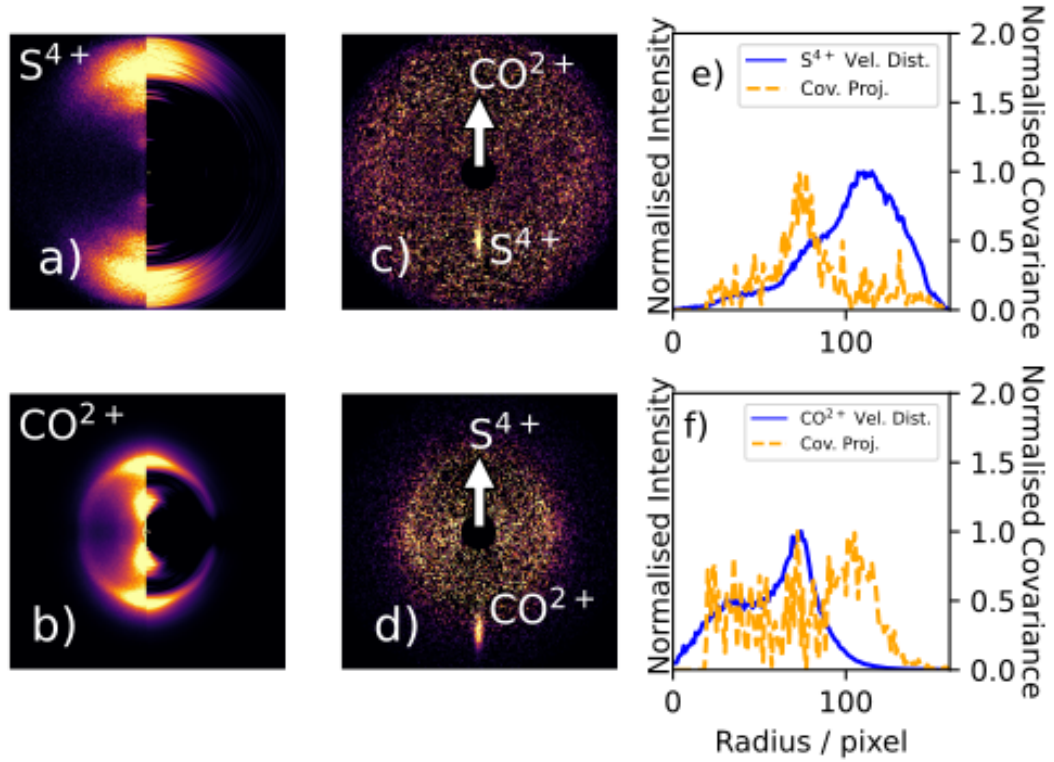


Figure 8.13: Recoil-frame covariance analysis of the CO^{2+} and S^{4+} ion pair. Panels a) and b) show the respective VMI images. Panels c) and d) show the recoil-frame angular covariance maps. Panels e) and f) show the velocity projections of the covariance map in comparison to the ion velocity distribution.

Coulomb explosion pathway.

8.5 Coulomb Explosion Dynamics at High pulse energy

This section investigates the Coulomb explosion of OCS at a pulse energy of $300\ \mu\text{J}$, over 41,140 laser shots.

8.5.1 Time-of-Flight Analysis

Figure 8.14 shows the mass spectrum following the Coulomb explosion of OCS at a pulse energy of $300\ \mu\text{J}$. The blue trace shows the average mass spectrum and the orange trace shows a magnified mass spectrum.

The mass spectrum is qualitatively similar to that obtained at a pulse energy of

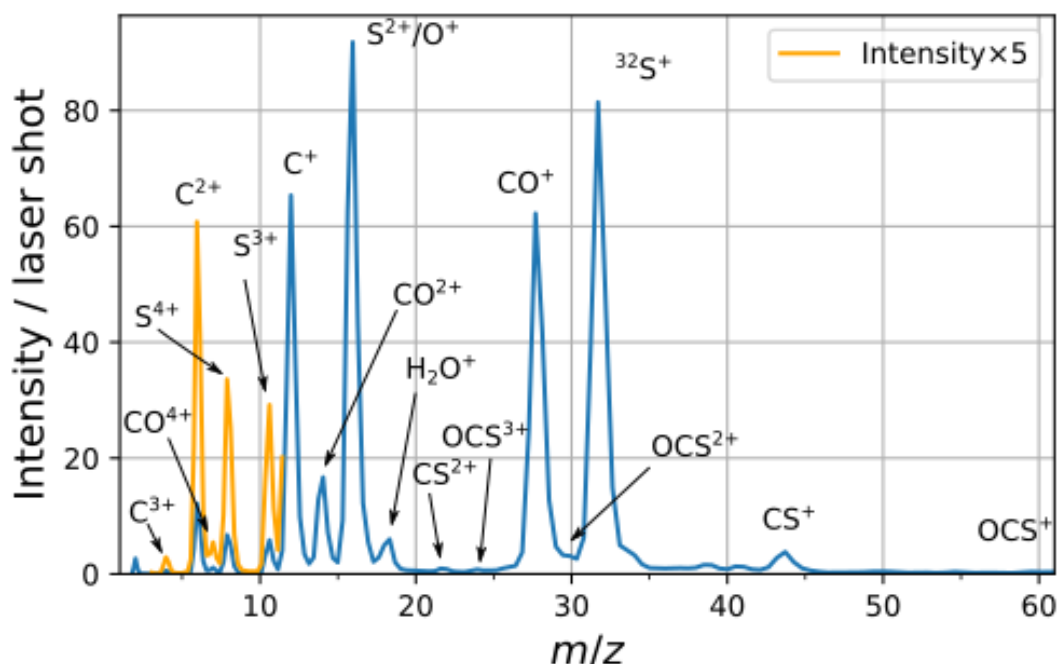


Figure 8.14: Average mass spectrum obtained following the Coulomb explosion of OCS. The mass spectrum was determined by calibrating the Time-of-Flight spectrum determined after centroiding the raw PImMS2 data. Ion peaks are labelled. Orange trace shows a magnified part of the mass spectrum for ions of low intensity.

300 μ J (see Figure 8.9). The only appreciable ion enhancement observed in the mass spectrum is the C^{3+} ion (charge degenerate with the O^{4+} and S^{8+} ions), which is still a very minor ion channel. The yield of the CO^{n+} ions is decreased. This is consistent with increased ionisation of the OCS molecules, resulting in further fragmentation or ionisation of the CO moiety. This is mirrored in the yields of the O^{n+} and C^{n+} . Increased ionisation is observed indirectly in a decrease in ion yield of the S^+ ions.

8.5.2 Coulomb Explosion Dynamics

Many of the Coulomb explosion dynamics observed at this pulse energy were also observed at lower pulse energies. Therefore these will not be discussed in great detail in this section. For completeness, Table 8.1 summarises the Coulomb explosion pathways observed at different pulse energies, throughout this Chapter.

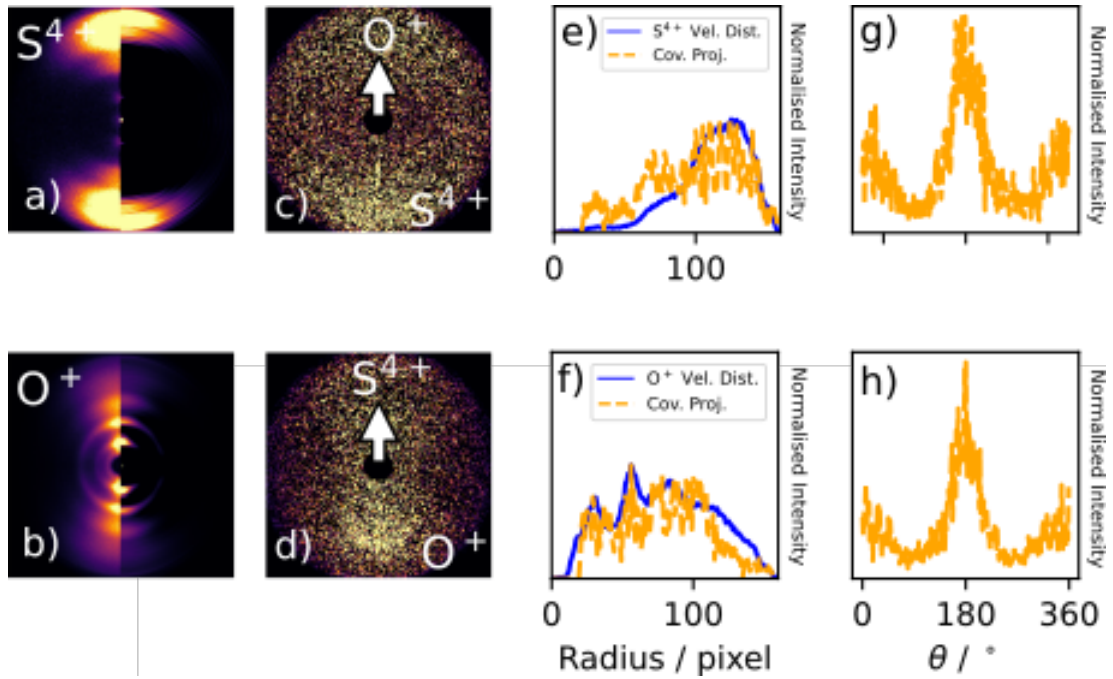


Figure 8.15: Recoil-frame angular covariance analysis of the S^{4+} and O^+ pair. Panels a) and b) show the centroided crushed image (left side) and inverted image (right side) for the S^{4+} and O^+ ion, respectively. Panels c) and d) show $\text{Cov}(O^+, S^{4+})$ and $\text{Cov}(S^{4+}, O^+)$. Panels e) and f) show a comparison of the velocity projection of the covariance map and the velocity distribution. Panels g) and h) show the radial integration of the covariance map to quantify how the covariance changes with angle. Radial range of integration was set over the peak in the velocity projection. See text for more details.

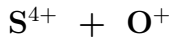


Figure 8.15 shows the recoil-frame angular covariance analysis for the S^{4+} and O^+ ion pair. Figure Panels 8.15 a) and 8.15 b) show the crushed and inverted image of the S^{4+} and O^+ ions, respectively. The velocity distribution of each ion is similar to those obtained at pulse energies of $200 \mu\text{J}$. Figure Panels 8.15 c) and 8.15 d) show $\text{Cov}(O^+, S^{4+})$ and $\text{Cov}(S^{4+}, O^+)$, respectively.

In both recoil-frame angular covariance maps, there is a broad recoil in the opposite direction observed in the plotted ion. The velocity projection of the angular covariance maps are shown in Figure Panels 8.15 e) and 8.15 f). The peak velocity range in the projection of $\text{Cov}(O^+, S^{4+})$ (Panel 8.15 e)) aligns convincingly with the S^{4+} high velocity peak. A similar trend is observed in the corresponding O^+ velocity distribution toward higher velocities. The angular dependence is illustrated further in Figure Panels 8.15 g) and 8.15 h) which integrates the covariance map over the

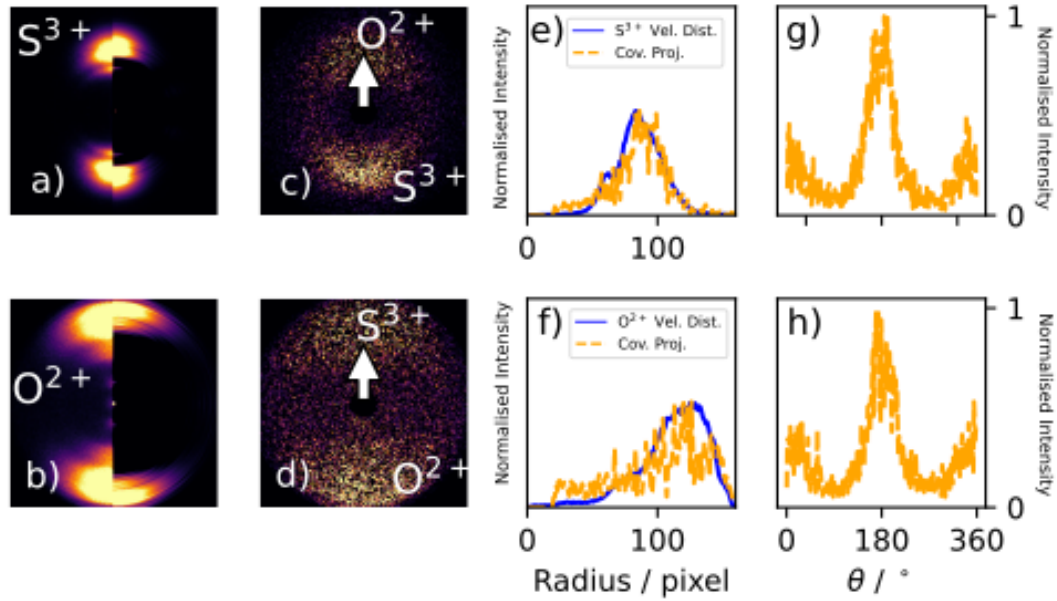


Figure 8.16: Recoil-frame angular covariance analysis of the S^{3+} and O^{2+} pair. Panels a) and b) show the centroided crushed image (left side) and Abel inverted image (right side) for the S^{3+} and O^{2+} ion, respectively. Panels c) and d) show $Cov(O^{2+}, S^{3+})$ and $Cov(S^{3+}, O^{2+})$. Panels e) and f) show a comparison of the velocity projection of the covariance map and the velocity distribution. Panels g) and h) show the radial integration of the covariance map to quantify how the covariance changes with angle. Radial range of integration was set over the peak in the velocity projection. See text for more details.

velocity range of interest. Both integrals are much more intense at $\sim 180^\circ$ relative to 0° and 360° . The broadness of the peak suggests that the recoil Coulomb explosion does not occur from an initially linear structure. This implies that the angle between the O and S atoms is deformed during the ionisation process. It is difficult to quantify the extent of the bending of the bond as this Coulomb explosion is still a three-body break-up due to the absence of the carbon atom. The ions described here could also be identified as the S^{2+} and O^{2+} ion pair through mass-to-charge degeneracy.



Figure 8.16 shows the equivalent plots for the S^{3+} and O^{2+} ion pair. This is a very similar break-up to the previously discussed break-up, except with a charge moved from the sulfur atom to the oxygen atom. Again, the recoil-frame angular covariance maps show an increased covariance at angles $\sim 180^\circ$ from the respective reference ions. This is illustrated in Figure Panels 8.16 g) and 8.16, h) which plot

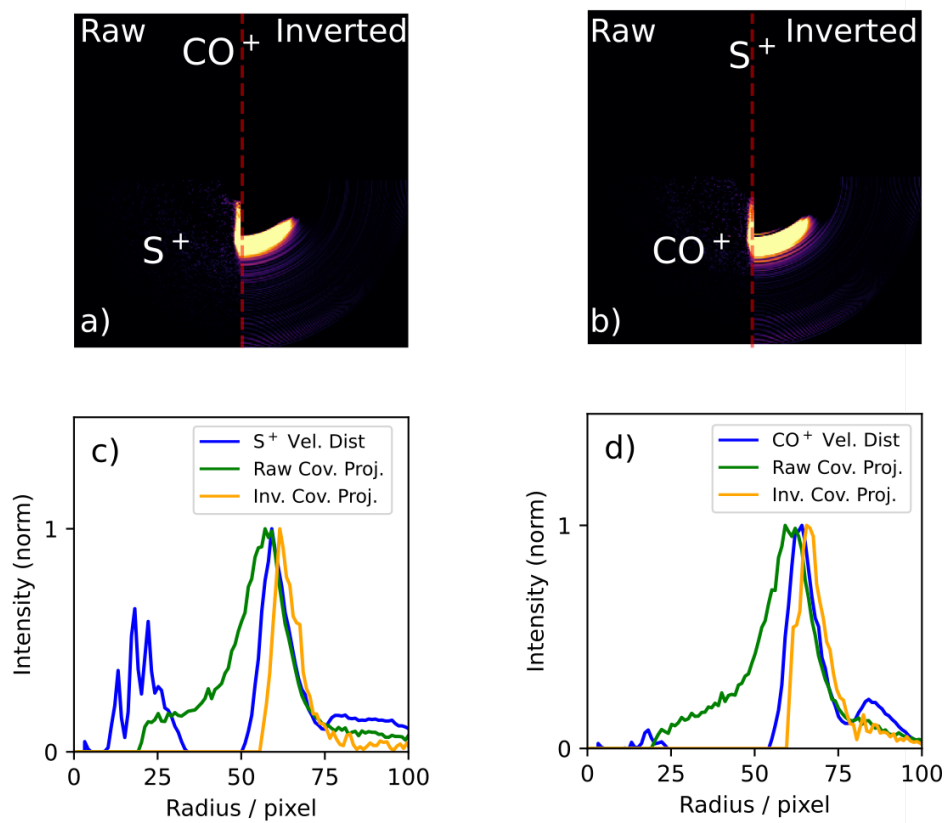


Figure 8.17: Panels a) and b) show the crushed (left) and inverted (right) covariance maps of $\text{Cov}(\text{CO}^+, \text{S}^+)$ and $\text{Cov}(\text{S}^+, \text{CO}^+)$, respectively. Panels c) and d) show the inverted velocity distribution of the plotted ion (blue), the raw covariance projection (green), and the inverted covariance distribution (orange). The inverted covariance peak is at least as sharp as the inverted velocity distribution.

the radial integral over the relevant velocity range. There is a clear enhancement at 180° relative to 0° and 360° . As with the previous ion pair, the angular distribution is relatively broad which further indicates that as these atoms are ionised and detached from the molecule, significant bending of the CO-S bond occurs.

8.6 Abel Inverted Covariance

As alluded to earlier in the Chapter, the calculated covariance projections tail toward lower velocities due to Coulomb explosions occurring outside the plane of the detector. 3D imaging could be used to employ 3D covariance to transform each pixel into a common vector and thence treat all ion events indiscriminately[60]. Unfortunately, the ion arrival time of the ions in these experiments is too short to

achieve this. Alternatively, the calculated covariance maps can be considered to be a crushed projection of the true covariance between two ions which must have an axis of cylindrical symmetry along the time-of-flight axis. Therefore inverting the crushed covariance maps reconstructs the relative momenta correlation between the two ions.

Figure 8.17 Panels a) and b) show the Raw (left) and Inverted (right) covariance maps, $\text{Cov}(\text{CO}^+, \text{S}^+)$ and $\text{Cov}(\text{S}^+, \text{CO}^+)$ for the CO^+ and S^+ ion pair recorded at a high laser intensity. The inverted covariance map has an arc of intensity. This is a result of using two Legendre polynomials used in the PBASEX algorithm[129]. The arc has a much narrow velocity spread than the Raw covariance map signature which extends to much lower radii. This is shown in Panels c) and d) of Figure 8.17 which compares the ion's velocity distribution to the raw and inverted covariance projection. For both ions, the projection of the inverted covariance map is equally as sharp as the inverted velocity distribution.

8.7 Radial-radial Covariance

This section demonstrates the application of radial-radial covariance to Coulomb explosion dynamics. Radial-radial covariance was introduced in Chapter 5 and provides information on correlations between the velocities of two different ions. This is indicative of the ion velocities following the Coulomb explosion process from which the ions were borne. Figure 8.18 shows the normal and partial radial-radial covariance maps for the CO^+ and S^+ (top row), S^{2+} (middle row), and S^{3+} (bottom row) ions following the Coulomb explosion of OCS at pulse energies of $300\mu\text{J}$. The left column shows the normal covariance maps and a covariance signature is visible in each covariance map there are substantial false correlations throughout the image, especially at around 60 pixels in the CO^+ radius.

The shot-by-shot yield of O^+/S^{2+} ions was used as the fluctuating parameter to calculate the partial covariance maps. This significantly reduces the false correlations and emphasises the true covariance signal. This covariance signal is a diagonal line centred at the velocity that each fragment gains from the Coulomb explosion. The diagonal line also arises from the projection of the covariance through the

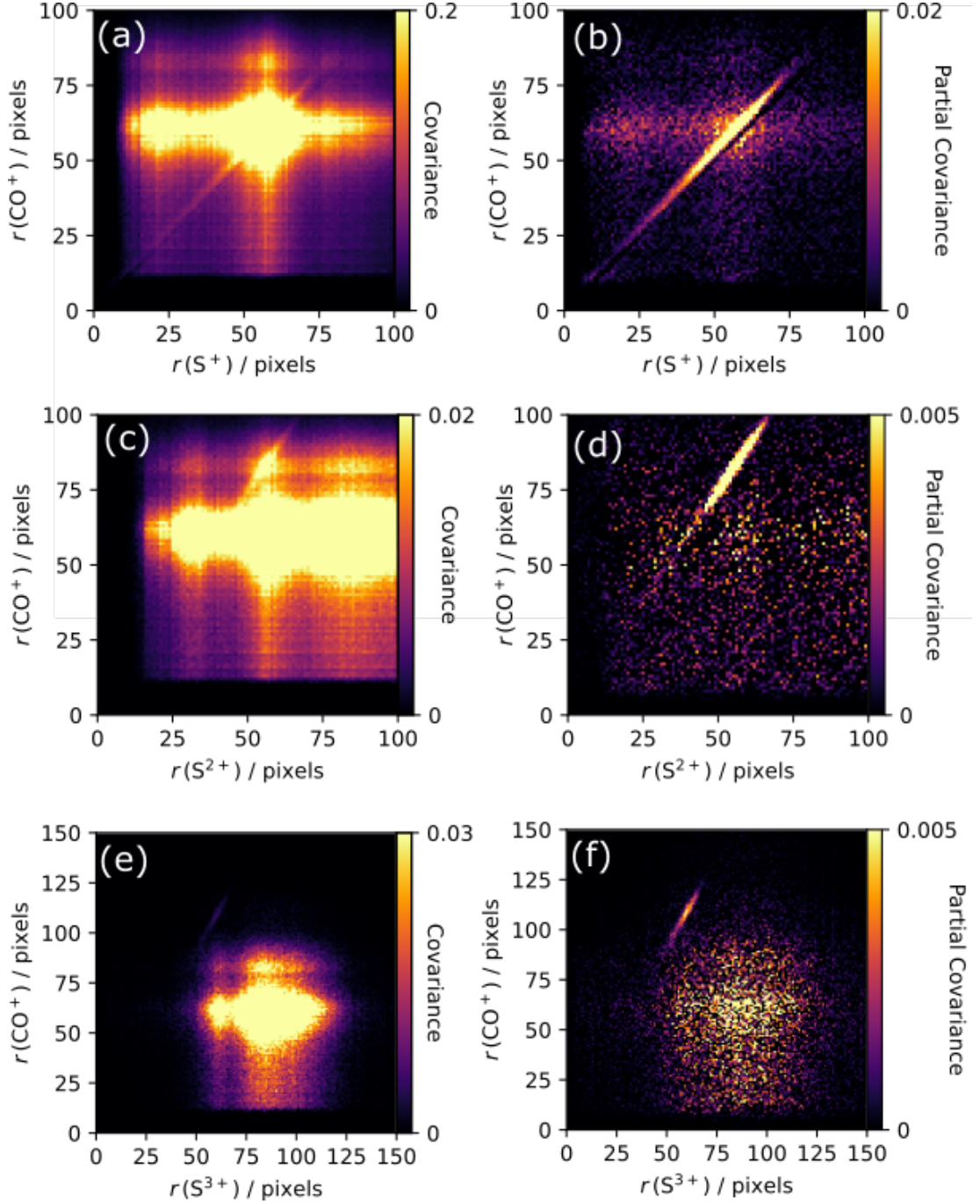


Figure 8.18: Normal and partial radial-radial covariance for the CO^+ and S^{n+} ions. Panels (a) and (b) show the normal and partial covariance map for the CO^+ and S^+ ion pair, respectively. Panels (c) and (d) show the normal and partial covariance map for the CO^+ and S^{2+} ion pair, respectively. Panels (e) and (f) show the normal and partial covariance map for the CO^+ and S^{3+} ion pair, respectively.

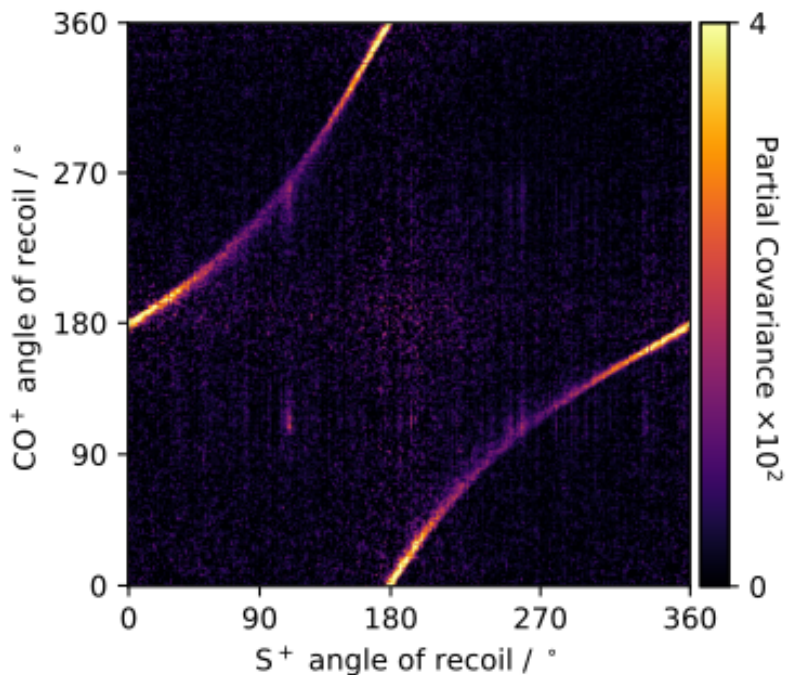


Figure 8.19: Partial covariance map of the recoil angle of S^+ and CO^+ ions.

Newton sphere. As expected, the radius of the CO^+ increases with increasing charge on the sulfur.

8.8 Angle-angle Covariance

Figure 8.19 shows the partial covariance map between the recoil angle of two ions, S^+ and CO^+ . Again, the shot-by-shot yield of O^+ and S^{2+} ions was used as the fluctuating parameter. The covariance map shows that when these ions are produced together the ions typically recoil along the polarisation axis (0° , 180° , and 360°). The relative angle of recoil has already been established through recoil-frame angular covariance. However, this covariance map shows that recoil does not occur perpendicularly to the polarisation of light and therefore retains information on the alignment of the molecules. This information is otherwise lost in recoil-frame angular covariance analysis, where recoil could be assumed to be isotropically back-to-back. The covariance appears to curve with angle of recoil, suggesting a non-back-to-back recoil. This is probably an artefact arising from

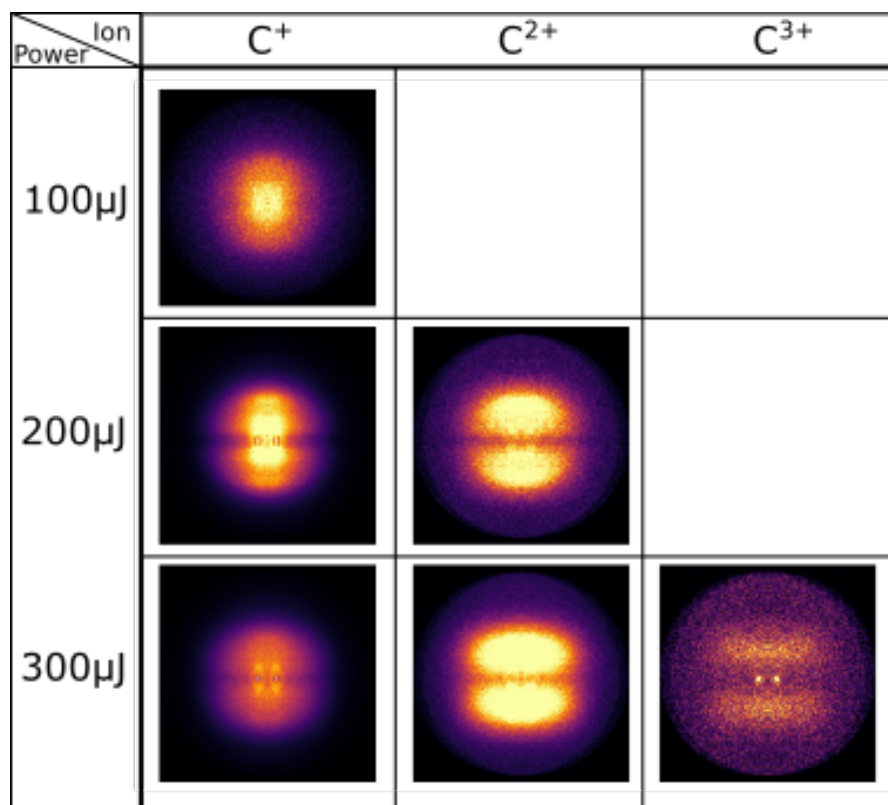


Figure 8.20: VMI images of carbon ions following Coulomb explosion of OCS at different pulse energies.

the non-circularity of the VMI images.

8.9 Carbon Ions

Carbon ions are always formed from at least a three-body break-up of OCS. Their ion images are interesting as the ion velocities are restricted by the two atoms on either side. As the ionisation and subsequent dissociation and fragmentation typically occurs along the polarisation of the electric field, the molecules that are ultimately detected are somewhat aligned in space. The VMI images for the C^{n+} ions are shown in Figure 8.20. C^+ ions are detected at all laser intensities investigated. There is a negligible yield of C^{2+} at 100 μJ per pulse and a negligible yield of C^{3+} at pulse energies less than 300 μJ .

The C^+ ions are mostly directed vertically in the page. There is significantly more intensity extending horizontally in the page in comparison with the other VMI

images that have been shown in this Chapter. This is a result of the carbon being situated between two charged ions and the ion trajectory is affected accordingly.

This trend is accentuated for more highly charged carbon ions as the charge on the oxygen and sulfur atoms are increased too further pushing the carbon away from them.

8.10 Discussion

From the strong-field induced Coulomb explosion dynamics OCS investigated in this Chapter, a number of things can be gleaned.

Firstly, with increasing laser intensity more highly charged parent ions are generated resulting in more highly charged fragments. Sulfur is more likely to be multiply charged than the carbonyl cofragment. This was evidenced in that no ion correlations were observed where the CO fragment was more highly charged than the sulfur fragment, e.g. $\text{Cov}(\text{CO}^{2+}, \text{S}^+)$ is not observed and has been reported previously[262, 263]. The Coulomb explosion pathway CS^+ and O^+ is readily observed. This is not typically observed in previous Coulomb explosion experiments of OCS though these were performed at much shorter pulse lengths (~ 6 fs) and therefore higher intensities, so an exact comparison cannot be made[263].

There is a propensity to not produce triply charged carbonyl ions as at all pulse energies there was a zero yield of this ion, despite an appreciable yield of CO^{2+} and CO^{4+} yield.

As the laser intensity was increased, a decrease in yields of singly charged species, S^+ and CO^+ and a general decrease of the CO^{n+} ions were observed. This is a result of more overall ionisation of the parent molecules and consequently more fragmentation.

Some ion velocity channels remain unidentified tho analysis. This is likely a result of not detecting the relevant cofragment as the final velocity is too large to be recorded on the detector at the current ion optic voltages. Future experiments could be performed at higher extraction voltages to capture the very high velocity ions. The most notable example is the CO^{4+} ion. This fragment can only be

Ion Correlations	100 μ J	200 μ J	300 μ J
S^+ / CO^+	✓	✓	✓
S^{2+} / CO^+	✓	✓	✓
S^{3+} / CO^+	×	✓	✓
O^+ / CS^+	✓	✓	✓
O^+ / CS^{2+}	×	✓	✓
S^{2+} / CO^{2+}	✓	✓	✓
S^{4+} / CO^{2+}	×	✓	✓
O^+ / S^+	×	✓	✓
O^+ / S^{2+}	✓	✓	✓
O^{2+} / S^{3+}	×	×	✓
O^+ / S^{4+}	×	×	✓

Table 8.1: Summary of the Coulomb explosion dynamics in OCS observed through covariance analysis at the pulse energies investigated.

partnered with a sulfur ion, yet no correlation was found between any sulfur ion, up to S^{4+} . Thus it is likely that a more highly charged sulfur ion exists that has not been detected or a velocity feature in the S^{4+} ion image is not detected. Currently, the Oxford VMI Spectrometer is limited by the high voltage supply that can be applied to the ion optic plates.

Table 8.1 summarises all the Coulomb explosion pathways observed in this Chapter at different pulse energies.

8.11 Conclusion

This Chapter has shown the advantages of covariance analysis at identifying Coulomb explosion pathways in a simple target molecule, OCS. Despite being a simple, linear, triatomic molecule, the Coulomb explosion dynamics are rich and are clearly very complicated with many pathways available. There is limited work in the literature regarding these dynamics and the work presented in this Chapter reveals much on the Coulomb explosion of OCS and adds to the prior work done. By using the statistical method of recoil-frame angular covariance analysis, ion momenta can be correlated to determine pathways. Often, this can be done accurately

enough to identify all velocity features present in an ion velocity distribution even in the complicated case of O^+/S^{2+} .

Through covariance analysis, OCS was found to Coulomb explode *via* a number of two-body pathways. Further, OCS shows a strong preference to fragment along the weaker carbon-sulfur bond rather than the carbon-oxygen bond. In pathways where there was an unequal charge distribution between fragments, the sulfur containing fragment was always found to hold the most charge. A number of three-body break ups were also observed through covariance analysis. This system would be a good candidate to observe three-fold angular covariance between the C^+ , S^+ , and O^+ ions. In three-fold angular covariance, the position of an ion, C^+ , is restricted to part of the ion image, and the covariance between the remaining ions is calculated. In this way, the correlations between O^+ and S^+ can be measured while the position of the carbon ion is known. This has the effect of orienting the molecule in three dimensions[264]. Successful three-fold covariance requires instances where three ions from the same process are detected in coincidence. This has a much smaller likelihood of occurring than two-fold coincidences. However, the high level of statistics and strong two-fold covariance signatures observed here suggest that these data sets would be suitable for this application.

Inverting angular covariance maps proved to be a valuable resource in sharpening the covariance signatures. Covariance analysis concluded that significant bending of the OCS molecule occurs during multiple sequential ionisation, resulting in non back-to-back recoil. Angle-angle and radial-radial covariance techniques were also utilised to show the covariance signatures in different ways.

9

Conclusions and Future Work

9.1 Summary

The 3D-imaging chapters in this thesis presented an experimental configuration for VMI experiments to implement a novel imaging technique, Post Extraction Inversion Slice Imaging (PEISI). This technique was characterised in Chapter 3 by investigating the model one-colour UV photodissociation of OCS in conjunction with the PImMS2 camera. At modest experimental conditions, the ion arrival time of CO^+ ions was increased by a factor of ten, in comparison to DC slicing conditions. This resulted in a highly-resolved extracted photofragment three-dimensional velocity distribution and improvements to the velocity resolution previously recorded in PImMS experiments[118]. The fidelity of the extracted velocity distribution allowed the entire VMI image to be expressed as an expansion of the modified spherical harmonics. Thus, the polarisation parameters, $m_{q\pm}^{\{k\}}$, that fully describe the photofragment angular distribution, can be determined immediately. This analysis can be used on systems that do not possess cylindrical symmetry in a single experiment. In Chapter 4, this was demonstrated by rotating the polarisation of photolysis light such that the electric field vector, ϵ , was no longer parallel to the detection plane and the cylindrical symmetry of the system was broken. Conventional VMI techniques, such as the inverse Abel transform,

are invalid methods for determining photofragment angular distributions under these conditions. However, by expanding the image in spherical harmonics, the angular distribution can be fully described. This technique would be immediately applicable to photofragment angular momentum polarization experiments, such as in the photodissociation of Cl_2 , where the distribution of the angular momentum is not symmetric about the photodissociation[15, 172]. Similarly, this technique could be readily adapted for use in crossed molecular beam scattering experiments where ion distributions are highly anisotropic[167–169].

The technique could become more comprehensive by incorporating improvements to the technique performed in mass spectrometry such as Double PEDA[265, 266] and time-dependent PEDA[63, 266]. Double PEDA employs two pulsed electric fields to focus Newton spheres of differing mass-to-charge ratio ranges, thereby increasing the number of ions that can be inverted, in general. Time-dependent PEDA changes the pulsed electric field strength with extraction time to cover a much larger m/z range[63]. In principle, these methods could be modified, in a similar way that has been done for single-field PEDA was, to become suitable for defocussing the temporal spread of photofragment Newton spheres. This would allow the extraction of high-resolution velocity distributions of ions across a wide m/z range. Simulations of optimal ion optic geometries and voltage variations using Simion[142] would be necessary to realise this.

PEISI could further be used in Coulomb explosion imaging experiments using the femtosecond laser experiment at Oxford (FLO). The obtainment of a highly accurate three-dimensional velocity distribution from PEISI experiments would allow for three-dimensional covariance to be employed, where each pixel of the Newton sphere is rotated (through two rotations) into a reference plane such that all pixels are directed along the same direction. This has the potential to provide full three-dimensional structural information of photodynamics[60].

A suitable model system for this experiment would be the Coulomb explosion of molecular iodine, I_2 . The mass-to-charge ratio of iodine is large enough that there should not be any temporal overlap with background ions such as water and nitrogen.

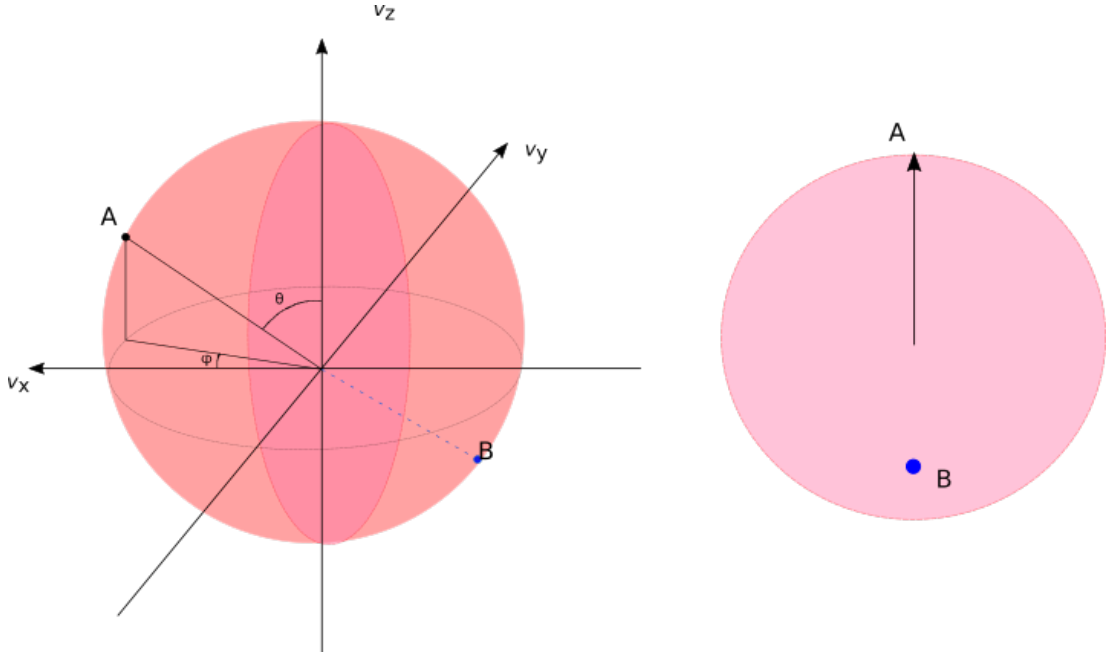


Figure 9.1: Concept of 3D covariance. The covariance is calculated between one pixel and all other pixels and repeated for all the other pixels. In two-dimensional recoil-frame angular covariance, each pixel's individual covariance map is then rotated so that each pixel lies in the same vector. In 3D covariance, the covariance maps are rotated in three dimensions such that the pixels again are directed along the same vector.

The Coulomb explosion dynamics will have simple covariance signatures for the proof-of-principle experiments. Figure 9.1 shows the detection of two fragments, *A* and *B*, recoiling 180° to one another, on opposite sides of the Newton sphere. The panel on the right shows the rotated covariance plane, equivalent to the shaded pink plane in the left panel and the arrow is equivalent to the v_z axis. In this cartoon, *B* would be expected to recoil in the opposite direction to *A*. This analysis method uses all the ion events usefully. For instance in two-dimensional recoil-frame angular covariance, if two ions recoil exactly parallel and anti-parallel to the ToF axis, the correlation between the two ions will not be properly captured as they will arrive at the same pixel, at different times of flight. In 3D covariance, both of these ions would be rotated such that correlation were recorded at the correct radius.

Further advancements to all the above can be made by increasing the timing resolution of that ion events are detected. Throughout this thesis, this was limited to the 25 ns timing resolution of the PImMS2 camera and was ultimately the limiting factor in further improving the quality of the data. The Timepix3Cam[52, 53] offers

a 256×256 pixel sensor array with a timing resolution of 1.56 ns. By incorporating a Timepix3Cam into the 3D imaging experiments, the timing resolution would in theory be improved tenfold and significant improvements would be made to the analysis thereafter. The drawback of this is that data accumulation could take longer to fully exploit the increased resolution. Another approach to increase the timing resolution is by fitting an analogue-to-digital current (ADC) readout to the back of the MCPs. An ADC readout converts the current of impinging ions at the detector into a digital signal. Theoretically, the MCPs have a timing resolution of < 1 ns. The digital signal can be coupled to the cluster size of ion events identified from the clustering algorithm of pixel events recorded by the PImMS camera. If the condition that digital signal scales linearly with cluster size is met (unpublished work, Felix Allum) then centroided PImMS events can be correlated to ADC signals and thereafter reassigned temporally according to the increased resolution of the ADC readout. Again, this method would greatly increase the resolution of these experiments.

Pump-probe Coulomb explosion imaging incorporating covariance analysis has been shown to be a valuable method for revealing complicated photodynamics. The UV photoexcitation and possible ring-opening of thiophenone was investigated in Chapters 6 and 7. The IR-probe investigation of the possible ring-opening and photodynamics of thiophenone suggested that a structural change consistent with ring-opening was observed through recoil-frame covariance analysis and velocity-dependent kinetic schemes. These experiments could be repeated at Oxford using FLO to perform high statistic, high quality pump-probe experiments to further investigate this in a more controlled manner than could be performed at FLASH during a high pressure beam time.

The measured recoil-frame angular covariance signature of ring-opening was observed in the $\text{CH}_x\text{O}^+/\text{C}_3\text{H}_x\text{S}^+$ ion pair. This could be confirmed by repeating the experiments with many more laser shots. The enhanced statistics could shed light on weaker channels that are also indicative of the isomerisation. The ring-opening is known to occur on a timescale of < 350 fs[18], by performing these

experiments with pump-probe delay steps of 100 fs, the ring-opening could be tracked on those timescales or a more accurate upper bound could be ascertained. Covariance imaging of VMI ion images has the benefit of revealing information on the fragmentation dynamics of photochemical processes. These experiments complement time-resolved photoelectron spectroscopy experiments which reveal information on the photoelectron energies and therefore the electronic states that are involved. This allows for a theoretical understanding of the photochemistry to be built, using high-level *ab initio* studies of the electronic structure and molecular dynamics calculations of the excited- and ground-state molecules. All experimental and theoretical studies combine to give the greatest understanding to these complex photochemical processes.

9.2 Future Directions

A future experiment that is planned with FLO is the UV photoisomerisation and Coulomb explosion of *cis*- and *trans*- isomers of 1,2-Dichloroethylene, $\text{C}_2\text{H}_2\text{Cl}_2$. These structural isomers should have different Coulomb explosion signatures on account of the positions of the respective chlorine atoms. In the *cis*-isomer, the chlorine atoms are on the same side of the atom and would be expected to recoil differently. Simulations of the Coulomb explosion of the two isomers were performed and Figure 9.2 shows the simulated recoil-frame covariance analysis for $\text{Cov}(\text{Cl}^+, \text{Cl}^+)$ (top row) and $\text{Cov}(\text{Cl}^+, \text{C}^+)$ (bottom) for *cis*-1,2-Dichloroethylene (left) and *trans*-1,2-Dichloroethylene (right). Similar covariance calculations following simulations of a Coulomb explosion break-ups have been successfully employed previously in the identification of structural isomers of difluoriodobenzene molecules[71, 267] and Coulomb explosion dynamics of a halogen-substituted cyanobiphenyl molecule[70]. Coulomb explosion dynamics were simulated by putting an average of four charges on the molecule with up a maximum one charge on each hydrogen, a maximum of two charges on each carbon, and no limit for each chlorine. The Coulomb explosion simulation was performed for 30,000 trajectories. Such experiments identifying absolute geometries have been performed using Coulomb explosion

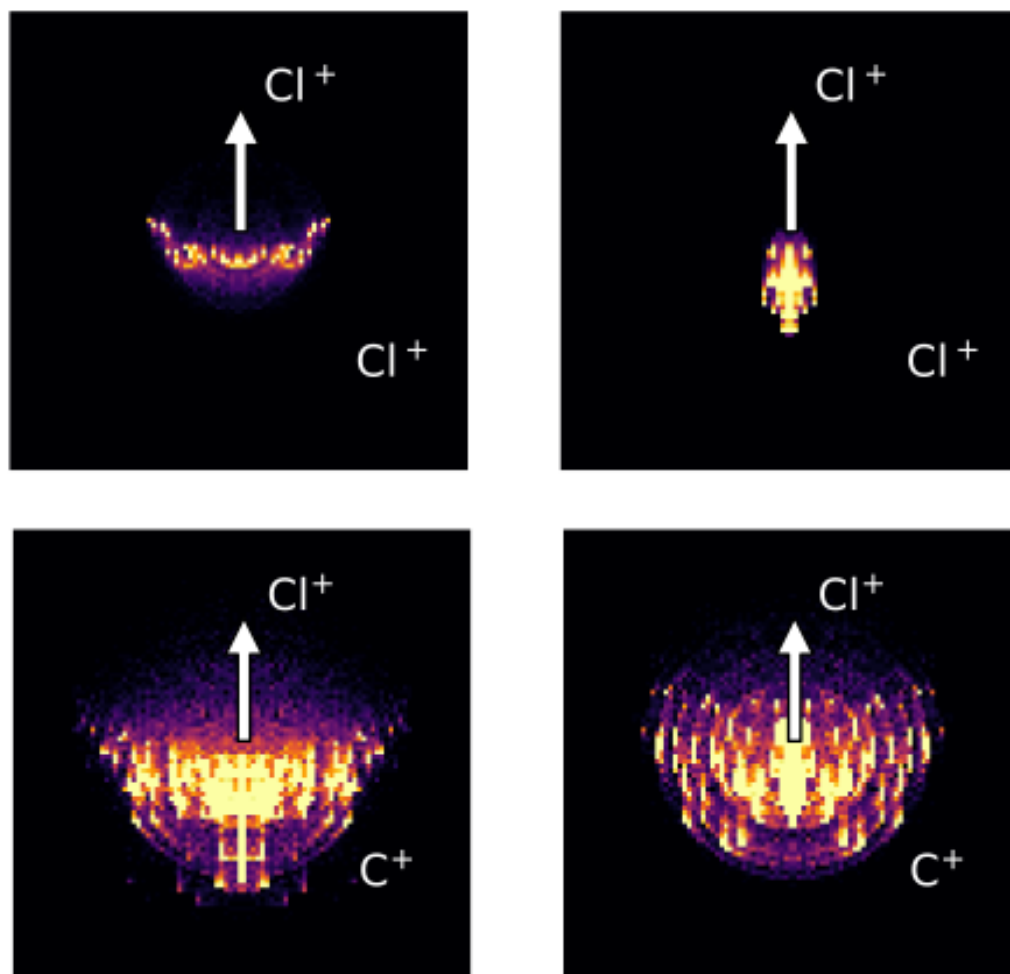


Figure 9.2: Simulated recoil-frame angular covariance maps, $\text{Cov}(\text{Cl}^+, \text{Cl}^+)$ (top row) and $\text{Cov}(\text{Cl}^+, \text{C}^+)$ (bottom) for *cis*- (left) and *trans*- (right) 1,2-Dichloroethylene following a Coulomb explosion.

imaging in coincidence [268, 269] and in covariance [58, 71]. However, this would be a particularly interesting system and signature to study as the isomers undergo UV-induced photoisomerisation[16]. Thus a pump-probe investigation into the photoexcitation dynamics could be performed while tracking substantial changes in the structure through delay-dependent covariance analysis.

The covariance signatures for $\text{Cov}(\text{Cl}^+, \text{Cl}^+)$ are markedly different for each isomer. The simulated covariance map for the *cis*-isomer shows the plotted chlorine ion momenta is directed in the same direction as the reference ion thus reflecting the structure of the molecule and the two carbon-chlorine bonds. Conversely, the

equivalent simulated map for the *trans*-isomer displays only back-to-back covariance: an indication that the two carbon-chlorine bonds are directed in opposite directions.

Similarly, the simulated covariance signatures in $\text{Cov}(\text{Cl}^+, \text{C}^+)$ are differentiable. In the *cis*-isomer, the covariance is a broad back-to-back signal with some sharp back-to-back covariance directed at 180° to the Cl^+ . Importantly, no covariance is observed in the same recoil direction as the Cl^+ ion. Again, by comparing this to the structure of the isomer, it is impossible for a carbon ion to be produced and recoil in the same direction as a chlorine ion. The two ions would always recoil in opposite directions. However, in the *trans*-isomer, it is possible for a carbon and a chlorine ion to recoil in the same direction as the chlorine atoms are on opposite sides of the carbon chain.

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Appendices

A

Appendix 1

This Appendix provides an introduction to the spherical harmonics and the mathematical framework for the spherical harmonic expansion. This mathematical technique is employed in Chapter 4 to describe VMI images as an expansion of spherical harmonics. This method is facilitated by the work described in Chapter 3. Post Extraction Inversion Slice Imaging is a method that greatly increases the temporal spread over which ions arrive at a two-dimensional position sensitive detector. This allows a high-resolution three-dimensional velocity distribution of the Newton sphere of ions to be extracted.

Spherical Harmonics

The spherical harmonics, are a special orthonormal set of polynomials in mathematics that are defined on the surface of a sphere used widely in the sciences. The spherical harmonics, termed $Y_k^q(\theta, \phi)$, are a function of polar angle, θ , and azimuthal angle, ϕ . The spherical harmonics can be further separated:

$$Y_k^q(\theta, \phi) = N_k^q P_k^{|q|}(\cos \theta) e^{iq\phi} \quad (\text{A.1})$$

where N_k^q is a normalisation factor and $P_k^{|q|}(\cos \theta)$ are the Associated Legendre polynomials.

Properties

Spherical harmonics have a number of properties that greatly simplify working with them[25]. This section will outline some important ones that will be used throughout this Appendix.

Normalisation

The spherical harmonics are normalised such that the integral between a harmonic, Y_k^q , and its complex conjugate, Y_k^{q*} , over the unit sphere is equal to unity:

$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} Y_k^q(\theta, \phi) Y_k^{q'*}(\theta, \phi) \sin \theta \, d\theta \, d\phi = 1 \quad (\text{A.2})$$

This leads to the normalisation constant, N_k^q , to be defined as:

$$N_k^q = \sqrt{(2k+1) \frac{(k-q)!}{(k+q)!}} \quad (\text{A.3})$$

Orthogonality

Further, the spherical harmonics are orthogonal on the surface of the unit sphere

$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} Y_k^q(\theta, \phi) Y_{k'}^{q'*}(\theta, \phi) \sin \theta \, d\theta \, d\phi = \delta_{k,k'} \delta_{q,q'} \quad (\text{A.4})$$

where $\delta_{i,i'}$ is the Kronecker delta. This is an important result that is utilised in the next section.

Spherical Harmonic Projection

It is mathematically proven that any function can be expressed exactly as a linear combination of spherical harmonics.

$$f(\theta, \phi) = \sum_{k=0}^{\infty} \sum_{q=-k}^{+k} a_{kq} Y_k^q(\theta, \phi) \quad (\text{A.5})$$

where a_{kq} are the corresponding coefficients for a given spherical harmonic, Y_k^q .

The coefficients, a_{kq} , can be calculated by integrating both sides of Equation (A.5) and using the orthogonality of the spherical harmonics:

$$a_{kq} = \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} f(\theta, \phi) Y_k^{q*}(\theta, \phi) \sin \theta \, d\phi \, d\theta \quad (\text{A.6})$$

The values of the a_{kq} coefficients calculated from Equation (A.6) can be substituted into Equation (A.5) to exactly describe the function.

Application to Ion Imaging

The spherical harmonics are relevant to ion imaging[15, 270] as they are fundamental in fully describing the photofragment angular distribution, PAD. Photofragments borne from the same process will broadly have the same initial speed and thus will form part of an expanding sphere with all other ions. The spatial distribution of these photofragments on the surface of the sphere may be described exactly by a spherical harmonic expansion. The coefficients, or moments, of the expansion have well-defined physical meanings. Conventionally, projections of the PADs are performed using modified spherical harmonics, $C_k^q(\theta, \phi)$, which are defined from the spherical harmonics, $Y_k^q(\theta, \phi)$ [270]

$$C_k^q(\theta, \phi) = \sqrt{\frac{4\pi}{2k+1}} Y_k^q(\theta, \phi) \quad (\text{A.7})$$

Equation (A.5) can be rewritten:

$$f(\theta, \phi) = \sum_{k=0}^{\infty} \sum_{q=-k}^{+k} m_{kq} C_k^q(\theta, \phi) \quad (\text{A.8})$$

where m_{kq} are analogous to the a_{kq} coefficients from Equation A.6 and are known as the polarisation moments. These are calculated analogously:

$$m_{kq} = \frac{2k+1}{4\pi} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} f(\theta, \phi) C_k^{q*}(\theta, \phi) \sin \theta \, d\phi \, d\theta \quad (\text{A.9})$$

where the factor of $\frac{2k+1}{4\pi}$ arises from the orthogonality of the modified spherical harmonics.

In general, these coefficients can be complex. This is inconvenient as the polarisation parameters are intended to give direct physical meaning in real three-dimensional space. This is overcome by transforming the complex parameters into real polarisation parameters using Hertol-Stoll normalisation[170]. The real

polarisation parameters do have real physical significance and quantify how much a distribution looks like its corresponding spherical harmonic. The transformation between complex and real polarisation parameters are:

$$m_{q+}^{\{k\}} = (-1)^q \sqrt{2} \text{Re}(m_{kq}), \quad q > 0 \quad (\text{A.10})$$

$$m_{q-}^{\{k\}} = (-1)^q \sqrt{2} \text{Im}(m_{kq}), \quad q > 0 \quad (\text{A.11})$$

$$m_0^{\{k\}} = m_{k0}, \quad (\text{A.12})$$

where $m_{q\pm}^{\{k\}}$ are the real polarisation coefficients.

As the complex polarisation parameters have been replaced with the real polarisation parameters, the function describing the PAD in Equation (A.8) is rewritten:

$$f(\theta, \phi) = \sum_{k=0}^{\infty} m_0^{\{k\}} C_0^{\{k\}}(\theta, \phi) + \sum_{q=1}^{+k} m_{q+}^{\{k\}} C_{q+}^{\{k\}}(\theta, \phi) + m_{q-}^{\{k\}} C_{q-}^{\{k\}}(\theta, \phi) \quad (\text{A.13})$$

where $C_{q\pm}^{\{k\}}$ are the real modified spherical harmonics, relating to the complex harmonics through the same transformation as for the real polarisation parameters.

$$C_{q+}^{\{k\}} = (-1)^q \sqrt{2} \text{Re}(C_{kq}) \quad (\text{A.14})$$

$$C_{q-}^{\{k\}} = (-1)^q \sqrt{2} \text{Im}(C_{kq}) \quad (\text{A.15})$$

Velocity Distribution

This method can be used to extract the velocity distribution of the image trivially. As the coefficient, $m_0^{\{0\}}(v)$, is independent of θ and ϕ , it is simply proportional to the number of ions at a given velocity. Therefore the velocity distribution is given by calculating $m_0^{\{0\}}$ as a function of the velocity, v .

$$P(v) = \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} f(\theta, \phi) C_0^{0*}(\theta, \phi) \sin \theta \, d\theta \, d\phi \quad (\text{A.16})$$

This is a very relation as it allows the velocity distribution to be extracted immediately. Further as the method uses the full three-dimensional PAD it does not rely on the central slice, a reconstructed image, or cylindrically symmetric data.

In VMI experiments, the time and position of a detected ion event is related to the initial velocity components of the ion. Theoretically, the full three-dimensional

velocity distribution can be extracted directly and transformed into the angular distribution which can be described by Equation (A.8). All the polarisation coefficients that describe the photofragment spatial distribution can be immediately calculated by evaluating the integrals in Equation (A.9). In order to achieve this experimentally, a highly-resolved velocity distribution is crucial. Post-Extraction Inversion Slice Imaging (PEISI) can provide a suitably well-resolved velocity distribution. The following section will investigate the expansion of a photofragment angular distribution from a simulated extracted velocity distribution under PEISI conditions using the Oxford VMI Spectrometer.

Simulated Photofragment Spatial Distributions

This section will discuss simulations performed to assess how possible it is to perform a spherical harmonic expansion of VMI images recorded under PEISI conditions.

Introduction

Simulated PImMS datasets were generated through ion trajectory simulations of CO^+ ions through the Oxford VMI Spectrometer using Simion 8.0[142]. The angular distribution of the CO^+ ions is determined by a set of polarisation coefficients, $m_{q\pm}^{\{k\}}$. This section will investigate whether the angular distribution can be fully reconstructed through a spherical harmonic expansions and determine any limitations.

The Simion simulation returns an (x, y) spatial coordinate at the detector, and a time-of-flight, t . Under VMI conditions, these are related to the initial velocity components that can be expressed in terms of a spherical coordinate system. In conventional imaging experiments (with linearly polarised light), the X –, Y –, and Z – axes are often defined as the direction of laser propagation, the time-of-flight direction, and the direction of laser polarisation, respectively.

$$v_X = f(x) \tag{A.17}$$

$$v_Y = g(t) \tag{A.18}$$

$$v_Z = h(y) \tag{A.19}$$

where (x, y) and t , are the pixel coordinates and the time-of-flight, respectively, the relations f, g, h are determined from the simulations and are typically linear relations, and v_i are the velocity in the laboratory frame components.

The velocity components can be expressed in spherical coordinates:

$$v_X = v \sin \theta \cos \phi \quad (\text{A.20})$$

$$v_Y = v \sin \theta \sin \phi \quad (\text{A.21})$$

$$v_Z = v \cos \theta \quad (\text{A.22})$$

where v is the speed, θ is the angle between an ion trajectory and the Z -axis, and ϕ is the angle between the projection of an ion trajectory on the XY plane and the positive X -axis.

The three-dimensional velocity distribution can therefore be rewritten as an angular distribution:

$$P(v, \theta, \phi) \sin \theta \, d\theta \, d\phi = P(v_x, v_y, v_z) \, dv_x \, dv_y \, dv_z \quad (\text{A.23})$$

Calculating Integrals

The integrals in Equation (A.9) that must be evaluated to determine the polarisation parameters were performed using Monte Carlo integration[271]. Monte Carlo integration is a form of numerical integration that uses random sampling of a function to numerically estimate a function. Although Monte Carlo integration is an inefficient method of integration in one dimension, it can be extended to multi-dimensional integrals at no extra cost. This is not true for efficient methods in one-dimension where efficiency drops exponentially when extra dimensions are introduced[271]. Further, in experimental data ion events appear randomly on the surface of the sphere which effectively predetermines the randomly sampled points that a Monte-Carlo integration requires.

As the integrals in Equation (A.9) are over two dimensions, Monte Carlo integration is an attractive option. By randomly sampling the sphere in $\cos \theta$

and ϕ , the integrals become:

$$I_k^q = \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} f(\theta, \phi) C_k^{q*}(\theta, \phi) d \cos \theta d \phi \quad (\text{A.24})$$

$$I_k^q = \frac{1}{N} \sum_{i=1}^N f(\theta_i, \phi_i) C_k^{q*}(\theta_i, \phi_i) \quad (\text{A.25})$$

$$m_{kq} = \frac{2k+1}{4\pi} I_k^q \quad (\text{A.26})$$

The polarisation parameters, m_{kq} , are scaled to m_{00} ,

$$m_{kq} = m_{kq}/m_{00} \quad (\text{A.27})$$

It should be noted that when $q = 0$, the modified spherical harmonics simplify to the ordinary Legendre polynomials.

$$C_k^0(\theta, \phi) = P_k(\theta) \quad (\text{A.28})$$

Recall from Equation (3.7), the anisotropy parameter, β , is defined in terms of the second Legendre polynomial. This parameter is therefore directly related to the modified spherical harmonics.

$$\beta = 2 \langle P_2(\cos \theta) \rangle = 2 \langle C_2^0(\theta, \phi) \rangle = 2m_0^{\{2\}} \quad (\text{A.29})$$

Results

Single Newton Sphere

The Newton sphere of a single CO photofragment following photodissociation of OCS at 230 nm with $v = 1480 \text{ m s}^{-1}$ was simulated under PEISI conditions in the Oxford VMI Spectrometer with a repeller voltage, $V_R = 500 \text{ V}$, a pulsed voltage, $V_P = 3 \text{ kV}$, and a switch time, $t_P = 4.117 \mu\text{s}$. Each ion trajectory was subsequently weighted according to a PAD with an anisotropy parameter, β , of 2 ($m_0^{\{2\}} = 1$) with no other contributions. A three-dimensional velocity distribution of the CO photofragment was extracted from the simulated detector positions through the relations in Equations (A.17), (A.18), and (A.19).

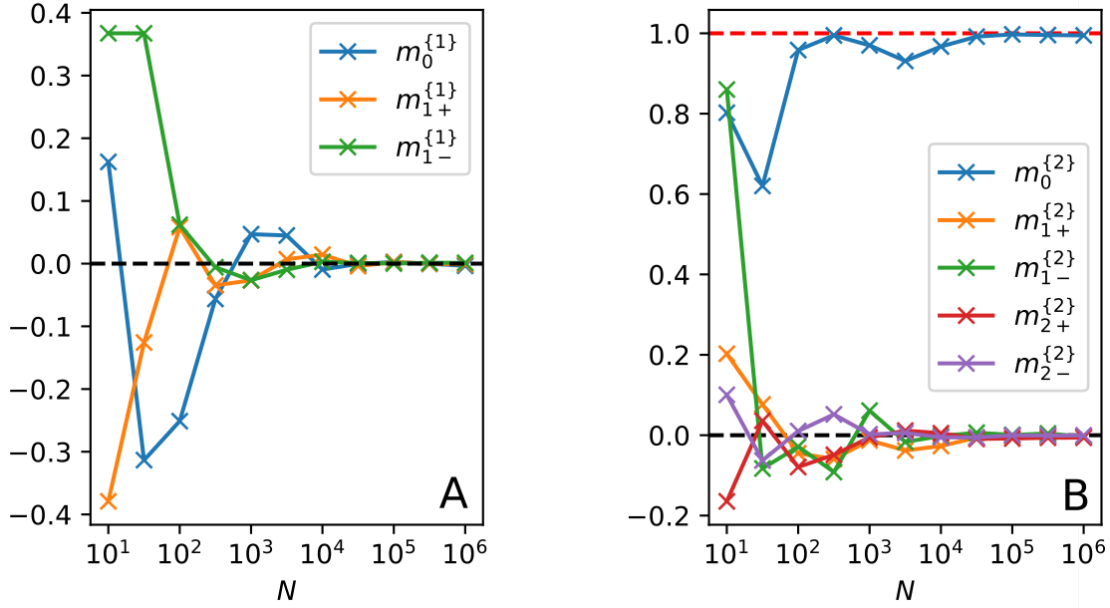


Figure A.1: Results of the spherical harmonic expansion of a single CO photofragment with a simulated β parameter of 2 ($m_0^{\{2\}} = 1$) with varying trajectories. Panel A and B show the ($m_{q\pm}^{\{2\}} = 1$) and ($m_{q\pm}^{\{1\}} = 1$), respectively. Each parameter is scaled such that ($m_0^{\{0\}}$) is equal to 1. The only contribution is calculated for $m_0^{\{2\}}$ at the correct simulated value. The coefficients begin to converge after $\approx 30,000$ trajectories.

The polarisation coefficients were calculated from the PAD by evaluating the Integrals in Equation (A.9) through Monte-Carlo integration and normalised according to Equation (A.27). This was performed for a number of ion trajectories. Figure A.1 shows the calculated coefficients as a function of N , the number of ion trajectories in the Monte Carlo integration. Panel A and B show the calculated $m_{q\pm}^{\{1\}}$ and $m_{q\pm}^{\{2\}}$ coefficients, respectively. The Monte Carlo integration converges on the simulated value for each coefficient after $10^{4.5}$ ($\approx 30,000$) shots. This shows that a spherical harmonic expansion of a VMI image recorded under PEISI conditions is sufficient to extract dynamical information from a single photofragment with an axis of cylindrical symmetry.

Nested Newton Spheres

This section will investigate a Newton sphere comprising two CO photofragments under the same PEISI conditions. The two photofragments are the CO photofragment from the previous section and a second CO photofragment with velocity,

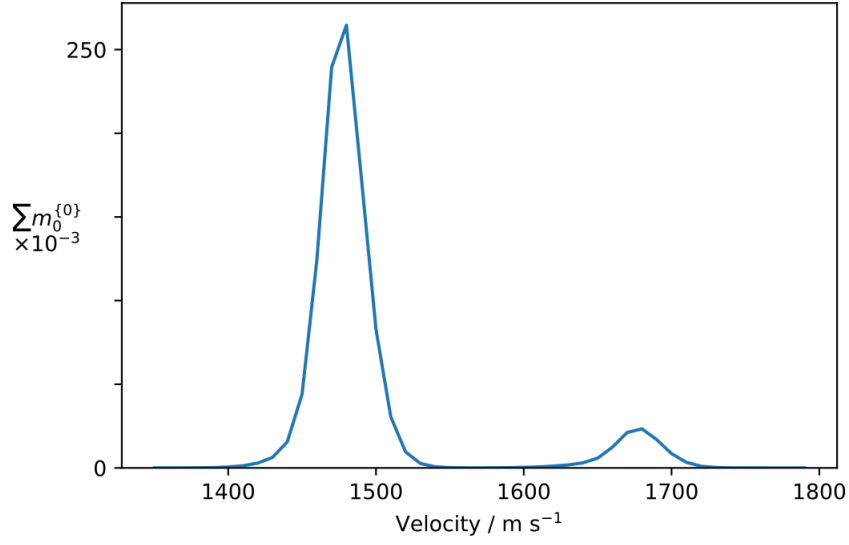


Figure A.2: The velocity distribution of a Newton sphere comprising two CO photofragments calculated by evaluating Equation (A.16).

$v = 1680 \text{ m s}^{-1}$ and an anisotropy parameter, β of 1 ($m_0^{\{2\}} = 0.5$) with no other contributions.

The velocity distribution can be extracted by evaluating Equation (A.16). The resulting velocity distribution is given in Figure A.2 obtained from a total of 1,000,000 CO trajectories. Each CO photofragment is uniquely resolved.

The photofragment angular distribution for each photofragment was determined from the total angular distribution by restricting the velocity to those of the respective CO photofragments:

$$P_i(\theta, \phi) = \int_{v_1}^{v_2} P(v, \theta, \phi) dv \quad (\text{A.30})$$

where i identifies the CO photofragment, and v_1 and v_2 correspond to the velocity range of the photofragment.

With the PAD for each CO photofragment determined, the polarisation parameters can be calculated by evaluating the integrals in Equation (A.9). Figure A.3 shows the calculated coefficients for each photofragment as a function of N , the number of CO trajectories. Panels (a) and (b) show the $m_{q\pm}^{\{1\}}$ and $m_{q\pm}^{\{2\}}$ coefficients for the Photofragment A, corresponding to the lower velocity photofragment. The $m_0^{\{2\}}$ coefficient is the only coefficient simulated to have a non-zero value ($m_0^{\{2\}} = 1$). The

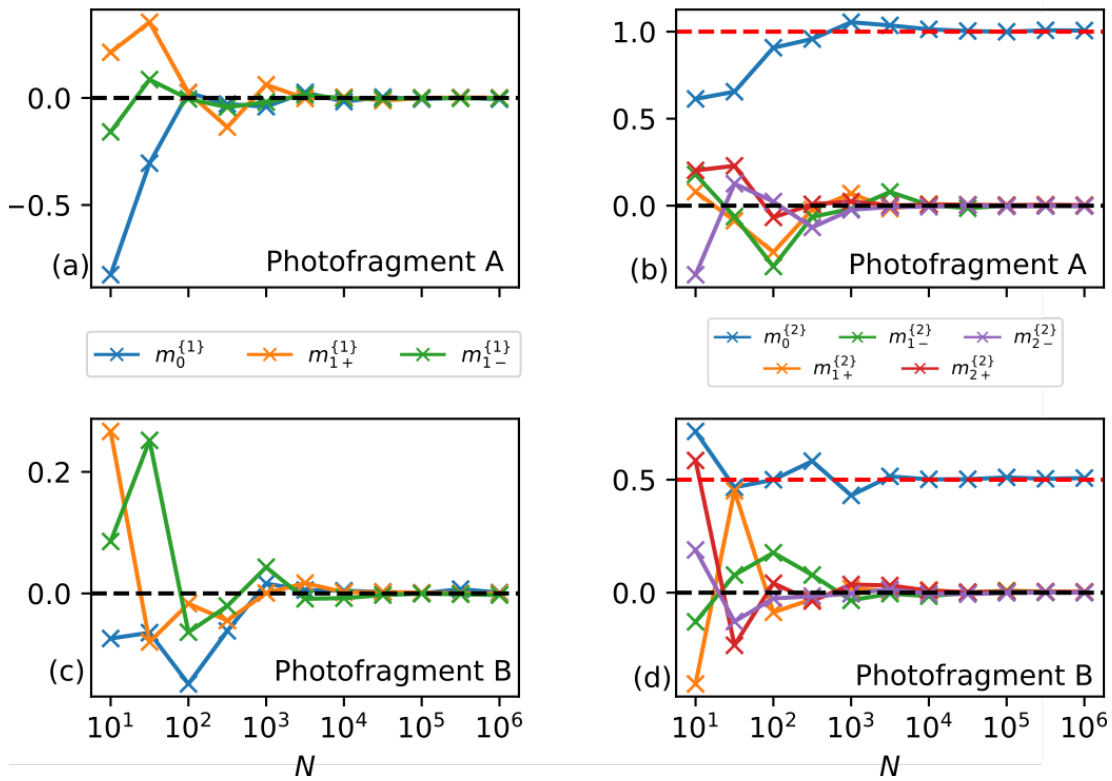


Figure A.3: Results of the spherical harmonic expansion of a Newton sphere containing two CO photofragments with simulated β parameters of 2 ($m_0^{\{2\}} = 1$) and 1 ($m_0^{\{2\}} = 0.5$) with varying trajectories. Panel A and B show the ($m_{q\pm}^{\{2\}} = 1$) and ($m_{q\pm}^{\{2\}} = 0.$), respectively. Each parameter is scaled such that $m_0^{\{0\}}$ is equal to 1. The only contribution is calculated for $m_0^{\{2\}}$ at the correct simulated value. The coefficients begin to converge after $\approx 30,000$ trajectories.

Monte Carlo integration converges on the simulated values after 10,000 trajectories. Panels (c) and (d) show the corresponding plots for the second photofragment. Again, the $m_0^{\{2\}}$ coefficient is the only coefficient simulated with a non-zero value (The $m_0^{\{2\}} = 0.5$). The Monte Carlo integration converges on the simulated values for all coefficients after $\approx 10,000$ trajectories.

The next section will investigate the simulation of the Newton spheres of CO($J = 50$) photofragments, following the UV dissociation at around 230 nm of OCS molecules either in the ground state, *A*, or with one quantum of energy in the vibrational bending mode, *B*, [150]. The resultant velocity ratio of these CO photofragments is 1.063 (the ratio of velocities from the previous section was 1.13). The simulated central slice images are shown in Figure A.4. The two CO

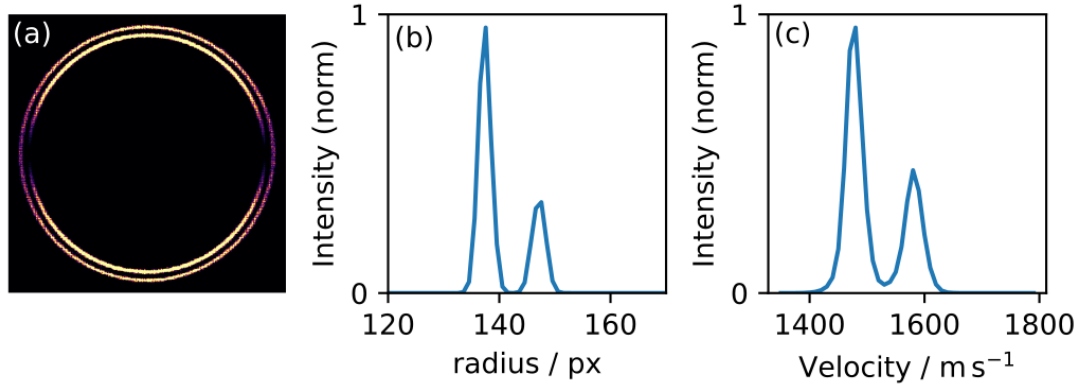


Figure A.4: Simulated data for a Newton sphere comprising two CO photofragments arising from different OCS molecules. Panel (a) shows the simulated central slice image as recorded by PImMS2. Panel (b) shows the radial distribution of the central slice image. Panel (c) shows the velocity distribution of the entire VMI image, calculated from Equation (A.16).

photofragments can be resolved in the central slice image in Panel (a). Panel (b) shows the radial distribution of the central slice image. Panel (c) shows the velocity distribution of the entire VMI image, calculated from Equation (A.16) and is in excellent agreement with the central slice velocity distribution. This method has the added benefit of using all the data in the image. The velocity distribution in (c) is slightly less well-resolved than the central slice velocity distribution as a result of velocity blurring when relating detector positions to initial velocity components.

The PADS for each photofragment, A and B, was determined through Equation (A.30) and the integrals in Equation (A.9) evaluated. Figure A.5 shows the calculated coefficients for each photofragment as a function of N , the number of CO trajectories. The top row shows the $m_{q\pm}^{\{1\}}$ and $m_{q\pm}^{\{2\}}$ coefficients for Photofragment A. The $m_0^{\{2\}}$ coefficient is the only coefficient simulated to have a non-zero value ($m_0^{\{2\}} = 1$). The Monte Carlo integration converges on the simulated values for all coefficients after 10,000 trajectories. The bottom row shows the corresponding plots for the second CO photofragment, B. Again, the $m_0^{\{2\}}$ coefficient is the only coefficient simulated with a non-zero value ($m_0^{\{2\}} = 0.5$).

Table A.1 summarises the simulated and calculated polarisation coefficients for each CO photofragment after 100,000 trajectories. The spherical harmonic

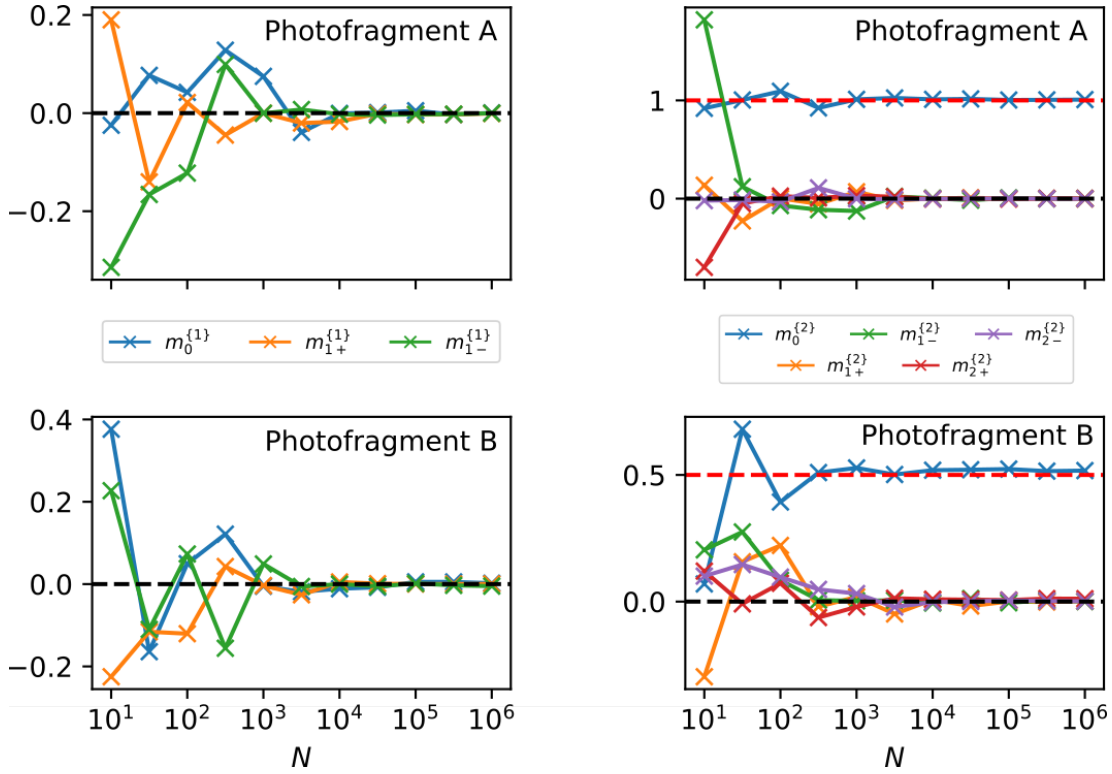


Figure A.5: Results of the spherical harmonic expansion of a Newton sphere comprising CO($J = 50$) photofragments arising from the UV dissociation at around 230 nm of OCS molecules either in the ground state or with one quantum of energy in the vibrational bending mode, with varying trajectories. Each photofragment had a simulated β parameter of 2 ($m_0^{\{2\}} = 1$) and 1 ($m_0^{\{2\}} = 0.5$), respectively. The top row shows the ($m_{q\pm}^{\{2\}} = 1$) and ($m_{q\pm}^{\{2\}} = 0.$) coefficients for the CO with lower velocity, photofragment A. The bottom row shows the ($m_{q\pm}^{\{2\}} = 1$) and ($m_{q\pm}^{\{2\}} = 0.$) coefficients for the CO with a higher velocity, photofragment B. Each parameter is scaled such that $m_0^{\{0\}}$ is equal to 1. The only contribution is calculated for $m_0^{\{2\}}$ at the correct simulated value. The coefficients begin to converge after $\approx 30,000$ trajectories.

expansion for photofragment A calculates the coefficients very accurately. The corresponding expansion for photofragment B also agrees very well with the simulated values though performs slightly more poorly. The calculated value for $m_0^{\{2\}}$ is slightly overestimated at 0.528 in comparison with the simulated value of 0.5. There is a similar overestimate (underestimate) for the $m_{2+}^{\{2\}}$ ($m_{1-}^{\{1\}}$) coefficients. The cause of these is contamination of the PAD for photofragment B with photofragment A. In total, the PAD corresponding to photofragment B contained $\approx 2,000$ A photofragments out of 100,000. This is a result of the discretisation of detecting ion events to a pixel or timebin precision and the corresponding convolution. This

k	$q\pm$	A		B	
		$m_{q\pm,\text{sim}}^{\{k\}}$	$m_{q\pm,\text{SHE}}^{\{k\}}$	$m_{q\pm,\text{sim}}^{\{k\}}$	$m_{q\pm,\text{SHE}}^{\{k\}}$
0	0	1	1	1	1
1	0	0	-0.002	0	0.001
1	1+	0	0	0	-0.001
1	1-	0	0.002	0	-0.020
2	0	1	1.002	0.5	0.528
2	1+	0	-0.001	0	-0.001
2	1-	0	0.001	0	-0.002
2	2+	0	-0.001	0	0.023
2	2-	0	-0.002	0	0

Table A.1: Simulated and calculated polarisation coefficients, $m_{q\pm}^{\{k\}}$, for a Newton sphere comprising two CO photofragments, A and B .

results in measured total velocities much different to the true velocity. As these photofragments have a different angular distribution they affect the spherical harmonic expansion. The same effect is less severe for the PAD for photofragment A as there is a greater simulated yield (see Panel (a) of Figure A.4) of this photofragment and therefore has a smaller effect.

The next section will briefly discuss a Newton sphere of ions comprising two CO photofragments resulting from the UV photodissociation of ground state OCS molecules in an isotopic ratio ($\text{OC}^{32}\text{S}:\text{OC}^{34}\text{S} \approx 1 : 24$). The resulting velocity ratio of CO photofragments is 1.014. Figure A.6 shows the velocity distribution (green) of the whole Newton sphere calculated from Equation (A.16). Also shown are the contribution of each individual CO photofragment. The most abundant CO photofragment (originating from OC^{32}S) (orange) and the minor CO photofragment (green) are very closely separated in velocity. Contamination of respective PADs is impossible to avoid for these ions under these PEISI conditions. A greater velocity resolution is necessary to resolve such photofragments. This could be improved through an increased timing resolution of recording ion times-of-flight, lower extraction voltages, increased PEISI voltages, or a larger pixel detector.

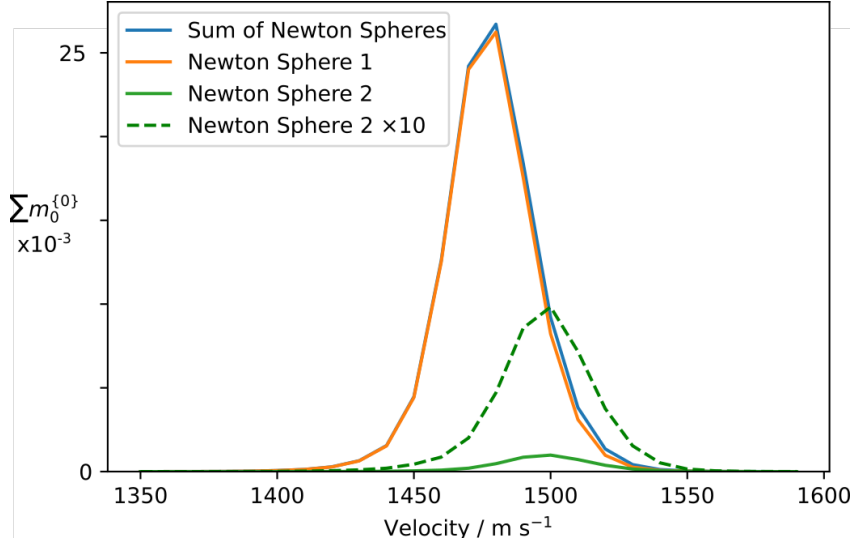


Figure A.6: The velocity distribution of CO photofragments resulting from OC^{32}S and OC^{34}S (blue). The individual velocity distributions are also shown. The photofragments cannot be resolved under these conditions.

Non-cylindrically symmetric Newton Sphere

Thus far, only systems with an axis of symmetry have been considered. This section will explore the potential to expand an ion image with no axis of symmetry as a combination of spherical harmonics. Slice imaging investigations can be performed to extract all anisotropy parameters though typically require at least three experiments with different photolysis polarisation geometries[15]. By recording the full 3D velocity distribution in PEISI imaging, the parameters can be derived by expanding the PAD in modified spherical harmonics in the same way as in previous sections. This obviates the need to perform multiple experiments and the polarisation coefficients can be extracted in a single experiment.

A model PAD was simulated with arbitrary polarisation coefficients, $m_{q\pm}^{\{k\}}$, up to $k \leq 2$:

$$f(\theta, \phi) = \sum_{k=0}^2 \sum_{q=-k}^{+k} m_k^q C_k^q(\theta, \phi) \quad (\text{A.31})$$

Simion 8.0[142] was used to simulate ion trajectories in the Oxford Spectrometer under PEISI conditions, as before. Each ion trajectory (θ, ϕ) was subsequently weighted with the model PAD according to Equation (A.31) and detailed in Table

k	$q\pm$	$m_{q\pm,\text{sim}}^{\{k\}}$	$m_{q\pm,\text{SHE}}^{\{k\}}$
0	0	1	1
1	0	0.1	0.010 ± 0.002
1	1+	-0.3	-0.299 ± 0.001
1	1-	0	0.004 ± 0
2	0	0.165	0.163 ± 0.002
2	1+	0.15	0.147 ± 0.001
2	1-	-0.2	-0.195 ± 0.001
2	2+	-0.15	-0.159 ± 0.001
2	2-	0.1	0.094 ± 0

Table A.2: Simulated and calculated polarisation coefficients, $m_{q\pm}^{\{k\}}$, for a Newton sphere comprising a photofragment with a non-cylindrically symmetric distribution.

A.2. The detected measurements of the ions were used to extract a measured PAD. The PAD was used to evaluate the Integrals (A.9) to calculate the real polarisation parameters.

Figure A.7 shows some of the results of the simulated photofragment. Panel (a) shows the simulated central slice image recorded at the detector. The lack of cylindrical symmetry can be seen as the intensity is not symmetric in the plane of the image. Panel (b) shows the angular distribution of intensity across the Newton sphere.

Table A.2 summarises the simulated and calculated polarisation coefficients for the photofragment. The calculated coefficients are in reasonable agreement with the simulated coefficients. The errors are standard errors from the Monte Carlo integration.

This section has shown that a spherical harmonic expansion of a simulated photofragment distribution with no axis of cylindrical symmetry recorded under PEISI conditions using the Oxford VMI Spectrometer can be used to fully extract the simulated polarisation parameters. This would be a very powerful technique were it to be confirmed experimentally. The next section will describe a modification to the photodissociation of OCS experiment that deliberately breaks an axis of symmetry.

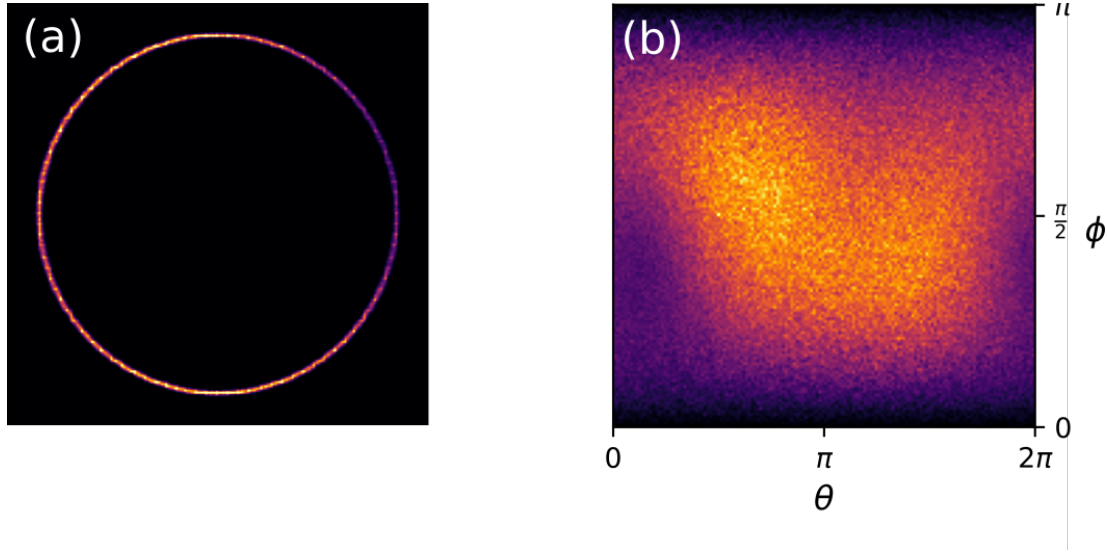


Figure A.7: Simulation of a photofragment with a non-cylindrically symmetric angular distribution. Panel (a) shows the simulated central slice image of the PAD described in Table A.2. Panel (b) shows the variation of intensity through the Newton sphere as a function of θ and ϕ . The highly irregular distribution can be seen in both panels.

System with a rotated axis of polarisation

To test the ability of performing a spherical harmonic expansion under PEISI conditions, an experiment was sought that could extract dynamical information in a way that would otherwise be impossible in conventional VMI. Thus far, all experiments that have been simulated, excluding the system with no cylindrical symmetry, could have used conventional VMI methods to obtain the same dynamical information. The central slice in the detector plane is all that is needed to describe the whole three-dimensional velocity distribution for a cylindrically symmetric PAD. An inverse Abel transform[126, 128] can be used to reconstruct the central slice of the velocity distribution from the crushed image at the detector. Alternatively, slice imaging[132, 270] can be employed to record only the part of the Newton sphere that the central slice occupies.

The approach chosen to test this was to rotate the axis of polarisation of the photolysis light by an angle of, α , and repeat the experiment. In this instance the cylindrical symmetry of the image is broken and conventional VMI methods cannot be used rigorously to extract dynamical information. If, for instance, an ion has a PAD corresponding to a β parameter of 2, fragments are preferentially trajected

parallel or anti-parallel to the molecular frame Z – axis. Ordinarily, this would result in a trajectory orthogonal to the time-of-flight and light propagation axes *i.e.* parallel to the detector plane and the laboratory frame Z' – axis. However, with the polarisation of light rotated by an angle, α , this is no longer the case. The ion will preferentially travel along the vector of the polarisation of light. As this vector is no longer parallel to the detector plane, the ion does not travel along the laboratory frame Z' – axis.

Cylindrical symmetry does still exist about the polarisation of light axis. Therefore for a fixed polar angle θ , (relative to the polarisation of light) the probability will not change as the azimuthal angle, ϕ is changed. With the detector plane parallel to the Z – axis, cylindrical symmetry is conserved. However, in the current set-up, the cylindrical symmetry is broken in the imaging plane as the polarisation of the light is no longer parallel to the detector plane. This experiment will be simulated in the next Section.

Approach

This section will outline the approach taken to perform the modified spherical harmonic expansion for a system with a rotated axis of polarisation. The multipolar expansion will only return the real polarisation parameters if the spherical coordinates, θ and ϕ , are defined correctly, otherwise the coefficients are rotated and do not possess any physical dynamical meaning. As discussed previously, and in Equations (A.20), (A.21), and (A.22), these are defined relative to the polarisation axis. As the velocity components, v_i , that are derived from the detector positions are relative to a coordinate system parallel to the detector plane, they must be transformed so that the Z' – axis is once again parallel to the axis of polarisation. (Note primed notation denotes laboratory frame coordinate system and un-primed denotes molecular frame coordinate system.)

Velocity coordinates can be transformed arbitrarily so that the Z' – axis is parallel to the polarisation axis using Rodrigues' rotation formula[102]:

$$\mathbf{v}_{\text{rot}} = \mathbf{v} \cos \alpha + (\mathbf{k} \times \mathbf{v}) \sin \alpha + \mathbf{k}(\mathbf{k} \cdot \mathbf{v})(1 - \cos \alpha) \quad (\text{A.32})$$

where $\mathbf{v}$ is the velocity vector to be rotated, α is the angle to be rotated, $\mathbf{k}$ is the unit vector describing the axis of rotation.

The axis of polarisation is rotated about the X' — axis as detailed previously and the plane of rotation is in the XZ plane. Mathematically this is equivalent to assigning the unit vector described in Equation (A.32) to:

$$\mathbf{k} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad (\text{A.33})$$

This simplifies Equation (A.32):

$$v_x = v_{x'} \quad (\text{A.34})$$

$$v_y = v_{y'} \cos \alpha - v_{z'} \sin \alpha \quad (\text{A.35})$$

$$v_z = v_{z'} \cos \alpha + v_{y'} \sin \alpha \quad (\text{A.36})$$

where the prime notation, i' denotes a coordinate system relative to the detector plane; x, y , and z are the axes to be used in the multipolar expansion; and α , is the angle of rotation. The x — component of the velocity does not change during the rotation. However, the y and z components do change.

Once this transformation is complete, the spherical coordinates that describe the PAD can be calculated in an identical way as described previously.

Simulated Images

Ion trajectories were simulated using Simion 8.0[142] and subsequently weighted according to a PAD with a β of 2, relative to the rotated polarisation axis. Panels A through D of Figure A.8 show the first four PImMS images recorded at the detector in the current set-up. A PAD with a β value of 2 has zero intensity when $\theta = \frac{\pi}{2}$, therefore the distribution may be thought of as being split in to two regions: one half where $\theta > \frac{\pi}{2}$ and another where $\theta < \frac{\pi}{2}$. One of these regions is rotated toward the direction detector and the other, away. The half rotated away from the detector will arrive at the detector first (due to the effect of the PEISI pulse). For a given rotation angle, α , the polar angle, θ , of the ions that arrive first at the detector

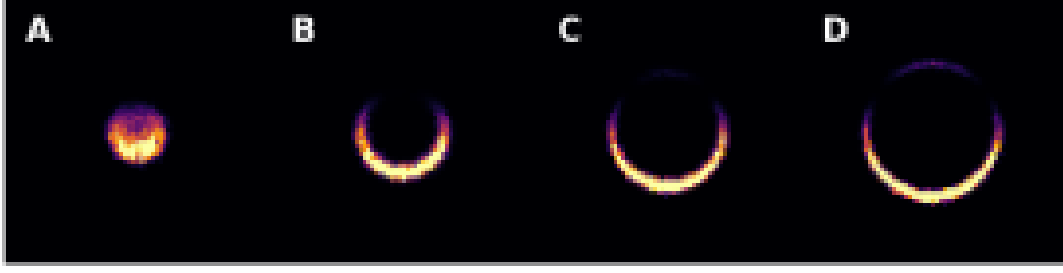


Figure A.8: Panels A through D show the first four slice images of simulated ions formed from interaction with photolysis light that has been rotated by an α ($=20^\circ$ in the simulation). See text for more details.

will vary (between $\frac{\pi}{2} \leq \theta \leq \pi$). For a rotation angle, $\alpha = 0^\circ$, or an unrotated polarisation axis, ions with θ values of $\frac{\pi}{2}$ will arrive first. For a rotation angle, $\alpha = 90^\circ$, a fully rotated polarisation axis, ions with θ values of 0 will arrive first.

In this simulation, the rotation angle, α was set 20° . The first ions to arrive are those with polar angles as close to $\frac{\pi}{2}$ as possible. These have the least probability in the PAD hence the low intensity ($P(\frac{\pi}{2}, \phi)=0$) in the image. The next ions to arrive will be those with larger θ angles from the same half of the distribution, the ‘backward’ ions. This will continue until polar angle of π is reached or the first ions of the second half, or ‘forward’ ions, of the distribution arrive.

This is shown in Figure A.8, Panel A shows the first recorded ion image (ions with $\theta \approx \frac{\pi}{2}$). Panel B and C show the subsequent images recorded. The radius of the image increases as a larger intersection of the Newton sphere is recorded. Panel D shows the first image where ions with polar angle, $\theta < \frac{\pi}{2}$, are recorded. This part of the image is relatively very weak in intensity due to the probability of an ion with its corresponding θ being close to zero, compounded by a large part of the sphere being cut in the first half of the image and a higher probability for those ions.

Figure A.9 shows a series of slice images recorded throughout the whole time-of-flight range. Here, the overall effect of the intensity inverting across the image as the time-of-flight increases is observed. It is clear that conventional VMI analysis techniques, such as slice or crushed imaging, are not valid here.

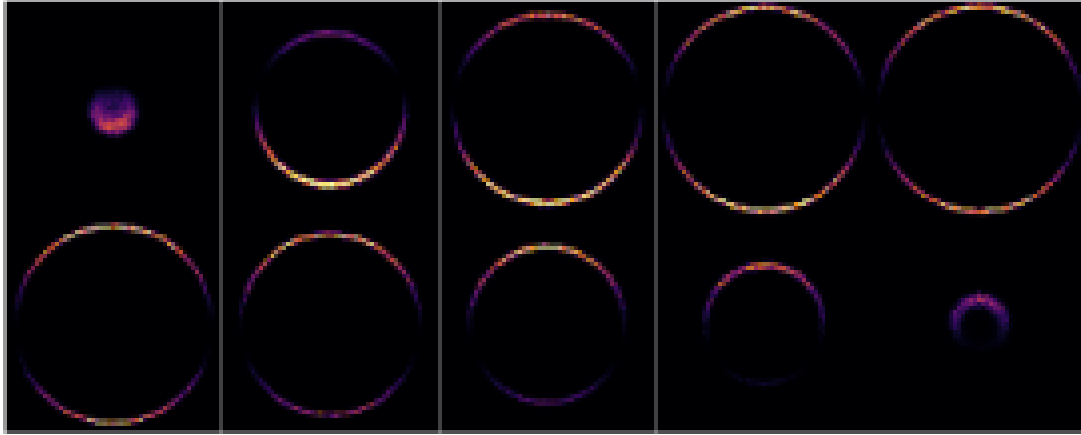


Figure A.9: Ten simulated slices recorded at the detector of the Oxford VMI Spectrometer in PEISI imaging. The key features of this experimental set-up can be seen: intensity appearing on one half of the image and gradually inverting in the second half of the time-of-flight peak.

Transforming the Velocity distribution

As discussed above, the velocities extracted from the detector must be transformed such that the Z' – axis is parallel to the polarisation of light. This means that part of the transformed Z' – component of velocity will also contribute some velocity to the original time-of-flight axis and part of the transformed Y – axis will contribute some of the original Z – component, as detailed in Equations (A.34), (A.35), and (A.36).

If the transformation is done correctly, slice images taken through the rotated Y – axis should resemble slices through the time-of-flight axis in conventional VMI. After the transformation of velocities, the angular distribution can be used in the spherical harmonic expansion.

Integrating over part of the Sphere

Spherical Harmonic Expansion

It may be the case that only part of the Newton sphere may be resolvable experimentally. This could arise if portions of two Newton spheres appear to overlap as a result of blurring from the detector. It would be desirable to be able to perform the expansion over a part of the ion distribution only, say the central slice or central cap of the Newton sphere.

The problem is that the modified spherical harmonic expansion relies on integrating over the whole sphere. The property of orthogonality ensures that the calculation of the coefficients in the expansion is greatly simplified:

$$\int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} C_{k'}^{q'}(\theta, \phi) C_k^{q*}(\theta, \phi) \sin \theta \, d\theta \, d\phi = \delta_{kk'} \delta_{qq'} \quad (\text{A.37})$$

When integrating over only part of the sphere, these integrals are not necessarily exact. To evaluate the above integral over the central part of a Newton sphere in the image plane, a change of variables is necessary:

$$\int_{-y}^{+y} \int_{\theta=0}^{\pi} C_{k'}^{q'}(\theta, \phi) C_k^{q*}(\theta, \phi) \sin \theta \frac{1}{v \sin \theta \cos \phi} \, d\theta \, dy \quad (\text{A.38})$$

where $\pm y$ are the y -coordinates to integrate between and the corresponding Jacobian is included. By choosing limits in y , the limits of integration represent vertical slices along the time-of-flight axis. This is convenient for ion imaging as PImMS discretisation serves as a natural slice.

The integrals can be done in sequence. However,

$$\int_{\theta=0}^{\pi} C_{k'}^{q'}(\theta, \phi) C_k^{q*}(\theta, \phi) \sin \theta \frac{1}{v \sin \theta \cos \phi} \, d\theta \neq \delta_{kk'} \quad (\text{A.39})$$

this means that

$$\int_{y=-y}^{+y} \int_{\theta=0}^{\pi} f(\theta\phi) C_k^{q*}(\theta, \phi) \sin \theta \frac{1}{v \sin \theta \cos \phi} \, d\theta \, dy \neq \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} m_k^q \delta_{kk'} \delta_{qq'} \quad (\text{A.40})$$

The important integral to evaluate is therefore

$$\int_{\theta=0}^{\pi} C_k^q(\theta\phi) C_{k'}^{q'*}(\theta, \phi) \sin \theta \, d\theta \quad (\text{A.41})$$

The value of this for some pairs of k, q and k', q' is zero but in general this is not the case. Therefore, the integral over all θ angles for a particular k', q' will in general give:

$$\int_{\theta=0}^{\pi} f(\theta\phi) C_k^{q*}(\theta, \phi) \sin \theta \, d\theta = \frac{2k+1}{4\pi} m_{kq} + A_{k_1 q_1} m_{k_1 q_1} + A_{k_2 q_2} m_{k_2 q_2} + \dots \quad (\text{A.42})$$

where $\frac{1}{2\pi}$ is the value of the integrand when $k = k'$ and $q = q'$, $A_{k_n q_n}$ are constants depending on the values of k and q , and m_{kq} are the respective polarisation parameters. If this part of the integral was further integrated over all ϕ angles, all

but the first term would vanish. However, as the integral over y does not cover the whole sphere, these terms will remain non-zero. Ultimately, the integral will evaluate to a linear combination of more than one complex polarisation parameters and not the reduced result.

Legendre Polynomial Expansion

A Legendre polynomial expansion of the data can be utilised in this case. As mentioned previously, the modified spherical harmonics simplify to the ordinary Legendre polynomials for $q = 0$. The Legendre polynomials are orthogonal over the interval $[-1, 1]$:

$$\int_{-1}^1 P_n(\cos \theta) P_m(\cos \theta) d \cos \theta = \frac{2}{2n+1} \delta_{m,n} \quad (\text{A.43})$$

where $\delta_{m,n}$ denotes the Kronecker delta.

This simplifies the problem as

$$\int_{-y}^{+y} \int_{\theta=0}^{\pi} f(\theta) P_k(\cos \theta) \sin \theta \frac{1}{v_x} d\theta dy = \int_{-y}^{+y} \sum_{k=0}^{\infty} \frac{2}{2n+1} u_k \delta_{k,n} dy \quad (\text{A.44})$$

$$u_k = \frac{2k+1}{2} \int_{-y}^{+y} \int_{\theta=0}^{\pi} f(\theta) P_k(\cos \theta) \sin \theta d\theta dy \quad (\text{A.45})$$

As each integral to calculate a u_k is over the same y range, this part of the integral will multiply the u_k by a constant factor which can therefore be ignored.

Thus it is possible to find the Legendre polynomial expansion of a distribution where the integral is performed over only part of the sphere. The drawback of this is that it will only work for cylindrically symmetric data. Also, this analysis could have equally have been performed with a Legendre polynomial expansion of just the central slice.

Spherical Harmonic Fitting

Another solution to this problem is to use a non-linear least squares fitting programme to fit data to the real and imaginary spherical harmonics, thus directly finding the real polarisation parameters. This may not find the exact coefficients but



Figure A.10: Parts of a Newton sphere with a $\cos^2 \theta$ distribution used to be fitted by the least squares fitting programme. Each portion of the Newton sphere reproduces the data well.

in cases where the expansion cannot be performed this is an effective method. Under the Spherical Harmonic Fitting approach, the photofragment angular distribution, $P(\theta, \phi)$, is fitted to Equation (A.13) to directly extract the real polarisation coefficients. This approach has the benefit that the entire Newton sphere does not have to be used to extract meaningful coefficients. This would be useful in situations where some parts of the Newton sphere may not be of high quality data. This could occur at the caps of the Newton sphere which are mapped onto the same part of the detector. In such scenario the conversion from detector positions to spherical angles, θ and ϕ , may not be accurate and would introduce errors into the spherical harmonic expansion. However, fitting two-dimensional data with $(2k + 1)$ variables is a challenging problem.

Conclusion

This Appendix has shown how the spherical harmonics are relevant to ion imaging and how PADs can be described as a sum of spherical harmonics - the coefficients of which can be calculated with a simple integral. These techniques have been tested thoroughly on purely simulated data and simulated PEISI experiments using the Oxford VMI Spectrometer.

An experiment designed specifically to break cylindrical symmetry and test the three-dimensional capabilities of this technique has been simulated fully with

expected results. In Chapter 4, these techniques will be tested on experimental data to investigate how this technique compares to simulations.