

Studies of Ultrafast Molecular Photofragmentation and Dynamics Using Fast Imaging Sensors

A thesis submitted for the degree of Doctor of Philosophy

Physical and Theoretical Chemistry



Kasra Amini

Merton College, University of Oxford

Hilary Term, 2017

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Abstract

In this thesis, the three-dimensional (3D) and multi-mass imaging capabilities of the Pixel Imaging Mass Spectrometry (PImMS) camera are demonstrated in a range of ion imaging experiments. The full 3D velocity distributions of the CO^+ and S^+ fragments, resulting from the photodissociation of OCS, are shown to be successfully captured with the PImMS camera by recording time-resolved slices through the full Newton sphere.

In the laser-induced Coulomb explosion of difluoroiodobenzene (DFIB) and dihydroxybromobenzene (DHBB) isomers, two- and three-fold covariance analysis revealed angular correlations between recoil ions, recorded by the PImMS2 camera, which were used to unambiguously identify structural isomers present in pure and mixed molecular beam samples. The Coulomb explosion imaging (CEI) technique and covariance analysis was extended to a femtosecond-resolved pump-probe study of the *trans-cis* isomerization in 4,4'-difluoroazobenzene (DFAB). Using a background-subtraction method, two-colour time-dependent features are extracted and are tentatively assigned to *cis*-DFAB with vibrationally hot *trans*-DFAB following $\text{S}_2 \leftarrow \text{S}_0$ excitation of vibrationally cold *trans*-DFAB.

The Coulomb explosions of laser-aligned and mixed-field oriented 2,6-DFIB molecules induced by strong-field or inner-shell ionization were found to be comparable, with only subtle differences observed. Using multi-photon inner-shell ionization with an ultrabright, femtosecond 11.6 nm free-electron laser probe pulse, high charge states of iodine in CH_3I and 2,6-DFIB are generated. The ensuing photodissociation, initiated by a 267 nm pump pulse, and charge transfer dynamics were observed in ‘real-time’ with the PImMS camera.

Publications

1. Three-dimensional imaging of carbonyl sulfide and ethyl iodide photodissociation using the pixel imaging mass spectrometry camera.

K. Amini, S. Blake, M. Brouard, M. B. Burt, E. Halford, A. Lauer, C. S. Slater, J. W. L. Lee, and C. Vallance, *Rev. Sci. Instrum.*, 2015, **86**, 103113.

2. Communication: Three-fold covariance imaging of laser-induced Coulomb explosions.

J. D. Pickering, K. Amini, M. Brouard, M. Burt, I. J. Bush, L. Christensen, A. Lauer, J. H. Nielsen, C. S. Slater, and H. Stapelfeldt, *J. Chem. Phys.*, 2016, **144**, 161105.

3. Jitter-correction for IR/UV-XUV pump-probe experiments at the FLASH free-electron laser.

E. Savelyev, R. Boll, C. Bomme, N. Schirmel, H. Redlin, B. Erk, S. Duesterer, E. Mueller, H. Hoepfner, S. Toleikis, J. Mueller, M. K. Czwalinna, R. Treusch, T. Kierspel, T. Mullins, S. Trippel, J. Wiese, J. Kuepper, F. Brausse, F. Krecinic, A. Rouzee, P. Rudawski, P. Johnsson, K. Amini, A. Lauer, M. Burt, M. Brouard, L. Christensen, J. Thøgersen, H. Stapelfeldt, N. Berrah, M. Mueller, A. Ulmer, S. Techert, A. Rudenko, D. Rolles, *New J. Phys.*, 2017, **19**, 043009.

4. Alignment, orientation, and Coulomb explosion of difluoroiodobenzene studied with the Pixel Imaging Mass Spectrometry (PImMS) camera.

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5. Isomer-dependent fragmentation dynamics of inner-shell photoionized difluoroiodobenzene.

U. Ablikim, C. Bomme, E. Savelyev, H. Xiong, R. Kushwahanah, R. Boll, B. Erk, K. Amini, T. Osipov, D. Kilcoyne, A. Rudenko, N. Berrah, D. Rolles, *Phys. Chem. Chem. Phys.*, 2017, **19**, 13419.

6. Probing the UV-Induced Photodissociation of CH₃I and C₆H₃F₂I with Femtosecond Time-Resolved Coulomb Explosion Imaging at FLASH.

E. Savelyev*, K. Amini*, F. Brausse, N. Berrah, C. Bomme, M. Brouard, M. Burt, L. Christensen, S. Düsterer, B. Erk, H. Høe ppner, T. Kierspel, F. Krecinic, A. Lauer, J. W. L. Lee, M. Müller, E. Müller, T. Mullins, H. Redlin, N. Schirmel, J. Thøgersen, S. Techert, S. Toleikis, R. Treusch, S. Trippel, A. Ulmer, C. Vallance, J. Wiese, P. Johnsson, J. Küpper, A. Rudenko, A. Rouzée, H. Stapelfeldt, D. Rolles, R. Boll, *Struct. Dyn.*, 2017.

7. Communication: Gas-phase isomer mixture identification using recoil-frame covariance imaging.

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8. Coulomb explosion imaging on concurrent CH₂BrI photodissociation dynamics.

M. Burt, R. Boll, J. W. L. Lee, K. Amini, H. Koeckert, C. Vallance, A. S. Gentleman, S. R. Mackenzie, S. Bari, C. Bomme, S. Düsterer, B. Erk, B. Manschwetus, E. Mueller, D. Rompotis, E. Savelyev, N. Schirmel, S. Techert, R. Treusch, J. Kuepper, S. Trippel, J. Wiese, H. Stapelfeldt, B. C. de Miranda, R. Guillemin, I. Ismail, L. Journal, T. Marchenko, J. Palaudoux, F. Penent, M. N. Piancastelli, M. Simon, O. Travnikova, F. Brausse, G. Goldsztejn, A. Rouzee, M. Geleoc, R. Geneaux, T. Ruchon, J. Underwood, D. M. P. Holland, A. S. Mereshchenko, P. K. Olshin, P. Johnsson, S. Maclot, J. Lahl, A. Rudenko, F. Ziaee, M. Brouard, D. Rolles, *Phys. Rev. A*, 2017.

Future Publications

1. Femtosecond-resolved electronic and nuclear structural change in CH_3I and CH_2ICl .
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2. Femtosecond-resolved Coulomb explosion imaging of CH_3I and CH_2ICl photodissociation dynamics.

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3. Investigation of CH_2BrI reaction dynamics using time-dependent Coulomb-explosion imaging on the femtosecond timescale

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4. Femtosecond-resolved dynamics in CH₂ICl at FLASH: a comparison between 266 nm and 800 nm initiated dynamics

K. Amini, R. Boll, M. Burt, H. Koeckert, J. W. L. Lee, C. Vallance, A. S. Gentleman, S. R. Mackenzie, S. Bari, C. Bomme, S. Duesterer, B. Erk, B. Manschwetus, E. Mueller, D. Rompotis, E. Savelyev, N. Schirmel, S. Techert, R. Treusch, J. Kuepper, S. Trippel, J. Wiese, H. Stapelfeldt, B. C. de Miranda, R. Guillemin, I. Ismail, L. Journal, T. Marchenko, J. Palaudoux, F. Penent, M. N. Piancastelli, M. Simon, O. Travnikova, F. Brausse, G. Goldsztejn, A. Rouzee, M. Geleoc, R. Geneaux, T. Ruchon, J. Underwood, D. M. P. Holland, A. S. Mereshchenko, P. K. Olshin, P. Johnsson, S. Maclot, J. Lahl, A. Rudenko, F. Ziaee, M. Brouard, D. Rolles, 2017.

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Chapter 1

Introduction

1.1 Introduction to Photochemistry

The excitation of molecules using high-intensity pulsed lasers leads to a rich variety of chemical transformations [1–3]. The rupturing of a chemical bond in a generic molecule AB, for example, can be achieved by exciting the molecule to an excited electronic state through the absorption of a photon (of energy $h\nu$) to generate two fragments, A + B. This is only one of a variety of outcomes that can befall an excited molecule, AB*, as shown in Figure 1.1 [1–3].

The excited molecule may undergo internal energy transfer processes to generate a new state AB[†] through, for example, intramolecular vibrational redistribution (IVR), internal conversion (IC) or intersystem crossing (ISC)[4–6]. In IVR (process (b) in Figure 1.1), energy is redistributed between vibrational quantum states in AB*. In IC and ISC, a transition occurs between electronic states of the same and different spin multiplicity, respectively. The excited molecule may also undergo isomerization (process c) or it may relax back down to its ground state through the emission of a photon with energy $h\nu'$ (process d), such as in fluorescence[7–9]. Depending on the photon intensity, one or more photons could also be absorbed by AB*; leading to its dissociation into A + B* (process e), its ionization to generate AB⁺ plus an electron (process f), or the production of an ion pair, A⁺ + B[−] (process g).

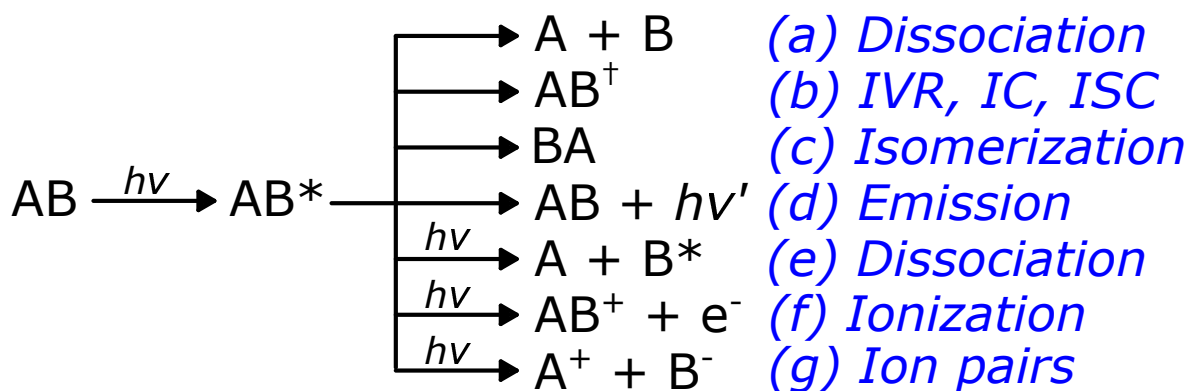


Figure 1.1: Various outcomes of exciting a molecule, AB , from its ground electronic state to its excited electronic state, AB^* , following the absorption of a photon with energy $h\nu$. Excitation of AB^* through the absorption of additional photons may also occur, as indicated by processes (e)–(g). See text for further details. This figure was adapted from Reference [3].

1.1.1 Photodissociation

Photodissociation can be categorized into several schemes, shown in Figure 1.2, and depends on the potential energy of the molecule in a particular geometry, described by potential energy curves (PECs) or surfaces (PESs) [1–3]. In all cases, a photon (of energy $h\nu$) promotes the molecule to an excited electronic state, AB^* . Direct dissociation of AB can occur if the molecule is promoted to an excited electronic state that is either repulsive or bound in character [1–3]. In the repulsive case, AB^* is rapidly dissociated. In the bound case, AB^* must possess energy greater than the dissociation limit to lead to direct dissociation.

If AB^* does not possess enough energy to overcome the dissociation threshold then dissociation may still occur through several indirect processes [1–3], shown in panels (c)–(f) of Figure 1.2. In panel (c), although AB^* lies below the dissociation threshold, it may be able to transition onto another nearby repulsive state *via* internal conversion or intersystem crossing. This is referred to as Herzberg type I or *electronic* predissociation. Panel (d) illustrates a Herzberg type II or *vibrational* predissociation. In this case, although AB^* lies above the dissociation limit, a barrier prevents the molecule from dissociating, keeping it in a quasi-bound state. To overcome this barrier, AB^* can undergo internal vibrational redistribution (IVR) to dissociate the molecule.

Herzberg type III or *predissociation by rotation* is illustrated in panel (e). Here,

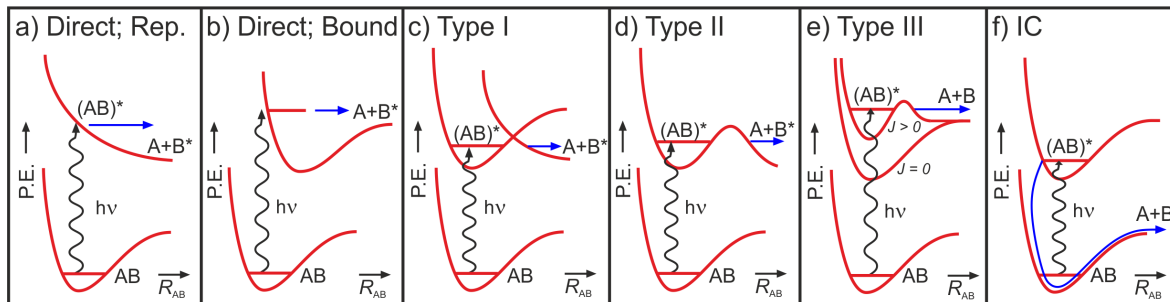


Figure 1.2: Several photodissociation schemes are presented for the following cases of a generic molecule $AB \rightarrow AB^*$: (a) direct dissociation *via* a repulsive state, (b) direct dissociation *via* a bound state, (c) Herzberg type I *electronic* predissociation, (d) Herzberg type II *vibrational* predissociation, (e) Herzberg type III *predissociation by rotation*, and (f) dissociation *via* internal conversion (IC). See text for more details. This figure was adapted from Reference [3].

non-rotating molecules can only dissociate if they are excited above the threshold to dissociation. However, in rotating molecules, a quasi-bound state with a barrier to dissociation may appear, which can be overcome by tunnelling through the barrier. In panel (f), AB^* lies below the threshold to dissociation on the excited state surface but may return to the ground electronic state *via* internal conversion (IC). If this transition occurs, then the molecule possesses enough energy to dissociate on the ground electronic state. Photodissociation, as well as many other photo-induced reactions, have been experimentally studied using the pump-probe scheme, details of which are given in the following section [10–12].

1.1.2 Pump-Probe Photodissociation

In the pump-probe scheme, a laser pulse interacts with the molecule to initiate the process of interest, such as photodissociation, and is called the “pump” pulse. The excited molecule is then ionized by a second pulse, referred to as the “probe” pulse, to generate one or more charged fragments. In Chapter 8, the photodissociation of methyl iodide (CH_3I) and 2,6-difluoroiodobenzene (DFIB, $\text{C}_6\text{H}_3\text{F}_2\text{I}$) were studied with ultraviolet pump and extreme-ultraviolet probe pulses.

The initial velocity distribution of the fragments after the photodissociation process can be preserved using the method of velocity-map [13] ion-imaging [14] (VMI). In VMI, ions with the same initial velocity are projected onto the same position (and at the

same time) on a position- and time-sensitive detector regardless of their initial starting position in the interaction region [13]. Further details of the technique are given in Chapter 3. Eppink and Parker first used the VMI technique to extract the speed and angular distributions of fragments following photodissociation of CH_3I around 240-334 nm and resonance-enhance multi-photon ionization (REMPI) [15, 16]. The photodissociation of CH_3I can be induced *via* *A*-band excitation from the bound ground state $X(^1A_1)$ to three repulsive excited states, as shown in Figure 1.3, which are: 1Q_1 , 3Q_0 and 3Q_1 [16]. The absorption cross-section for these three excited electronic states in the *A*-band are also shown in the inset of Figure 1.3. The strong parallel transition to 3Q_0 generates a methyl fragment, CH_3 , with a spin-orbit excited iodine, $\text{I}(^2P_{1/2})$, which is denoted as I^* henceforth. The weak perpendicular transitions to the 1Q_1 and 3Q_1 , on the other hand, generate a methyl fragment with a spin-orbit ground state iodine, $\text{I}(^2P_{3/2})$, which is denoted as I henceforth. A nonadiabatic curve-crossing from the 3Q_0 ($\equiv \text{I}^*$) state to the 1Q_1 ($\equiv \text{I}$) state can also occur. Eppink and Parker observed that the probability for curve crossing ($^3Q_0 \rightarrow ^1Q_1$) was reduced with increasing pump energy. The photon energy dependence of the curve crossing was further supported by the increased quantum yield for the I^* channel that was observed upon decreasing wavelength.

In a pump-probe study by Bañares and coworkers [17], the “reverse” nonadiabatic crossing ($^3Q_0 \leftarrow ^1Q_1$) was deduced at the blue edge of the *A*-band (217-230 nm). At 217 nm, the excitation of the ground state to the 1Q_1 state should dominate any other transition [18] (see inset in Figure 1.3). In their study, the anisotropy (β) parameter was investigated, which gives an insight into what type of transition occurs in the molecule: a purely parallel ($\beta = +2$), a purely perpendicular ($\beta = -1$), or a mix of both ($\beta \sim 0$). Since the 1Q_1 state is populated *via* a weak perpendicular transition, it was therefore expected that the value of β should be negative. However, even though the anisotropy parameter decreased with decreasing wavelength, it remained far from its limiting value for both I and I^* at 217 nm. Since the parallel transition to the 3Q_0 state from the ground state is negligible at 217 nm, this non-negative β value provided evidence for the reverse $^3Q_0 \leftarrow ^1Q_1$ nonadiabatic crossing [17].

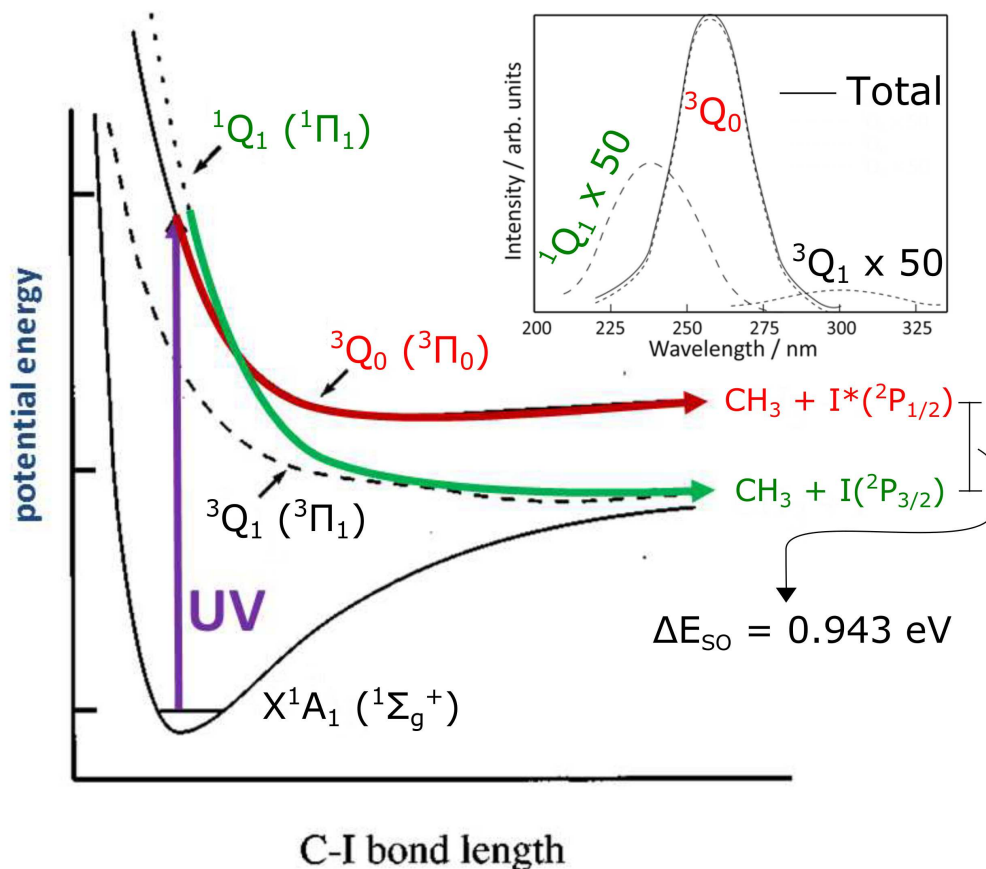
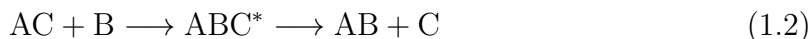
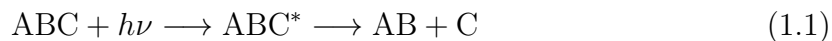


Figure 1.3: The potential energy surfaces involved in the *A*-band dissociation of CH_3I that are optically accessible with an ultraviolet photon. The ground (X^1A_1) and excited (1Q_1 (green), 3Q_0 (red), and 3Q_1 (black)) electronic states are shown, with the latter given in Mulliken notation[19]. The spin-orbit splitting of iodine in its spin-orbit ground (${}^2P_{3/2}$) and excited (${}^2P_{1/2}$) states is 0.943 eV[16]. The inset shows the absorption cross-section of the three excited electronic states in the *A*-band. Main figure was adapted from Reference [16], and the inset was adapted from Reference [20].

In a separate study by Eppink and Parker, the energy partitioning between translational and internal degrees of freedom in CH_3I was investigated by monitoring the iodine and methyl photofragments following dissociation of CH_3I in the UV region [15]. They observed vibrational structure in the kinetic energy distribution of both fragments, which suggests that vibrationally hot CH_3I molecules were photodissociated. At the red edge of the *A*-band (286–333 nm), Bañares and coworkers [21] also observed the appearance of vibrational structure in the kinetic energy distribution of the methyl photofragment after photodissociation. They showed that increasing the wavelength of the pump pulse lead to higher initial vibrational excitation of CH_3I , with a negligible contribution from the vibrational ground state observed at the highest wavelength of 333 nm [21].

Murdock *et al.* studied more complex systems, such as iodobenzene and their fluorinated compounds, in the UV region [22]. They showed that for these larger systems, additional (indirect) routes to the formation of a free iodine atom after photodissociation are possible. In particular, they showed that *electronic* predissociation from a bound excited state to a repulsive excited state were involved. These indirect routes are not observed in the alkyl halide case, such as CH₃I [16, 22].

In general, the process of unimolecular photodissociation has been termed a “half-collision” reaction (Equation (1.1)) since the same products can be generated as in a “full-collision” reaction (Equation (1.2)), in which two particles collide with each other [23–29].



The difficulty of carrying out time-resolved experiments on full-collisions is that it is challenging to determine the start time of the reaction (*i.e.* t_0). Whilst in photodissociation, a molecule with a well-defined geometry absorbs a photon to initiate the reaction of interest, and thus t_0 is known.

Figure 1.4 illustrates the time-dependent pump-probe scheme. Control over the delay between the pump (green arrow) and probe (blue arrow) pulses, referred to as τ , allows time-resolved pump-probe measurements to be recorded. By recording data at a series of τ , a “molecular movie” of the dissociation of AB* along the reaction coordinate can be generated. In the experiments discussed so far, nanosecond pulses are used which were not short enough in time to capture the nuclear dynamics of the photofragments in “real-time” following dissociation of the parent molecule. To investigate changes in the nuclear dynamics and electron dynamics of a molecular system, high-intensity ($> 10^{13} \text{W cm}^{-2}$) pulsed lasers are required that have a pulse duration on the timescale of nuclear motion (femtoseconds) and electron motion (attoseconds), respectively. Femtosecond [25, 30–33] and attosecond [34–39] pulse sources have been developed and employed in the the last 30 years, and many studies that employ time-resolved pump-probe schemes have been reported in the literature [25, 30–33, 39]. In

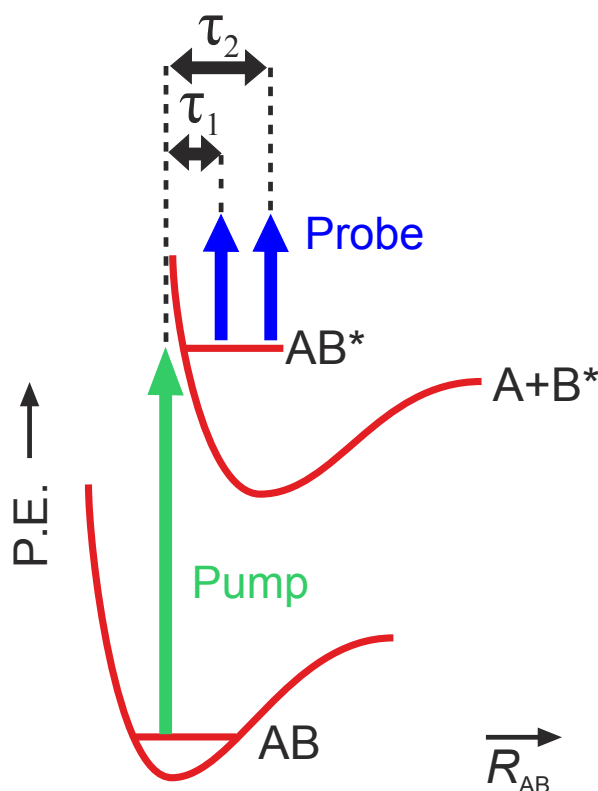


Figure 1.4: An illustration of the time-resolved pump-probe scheme. A “pump” pulse (green arrow) promotes AB to a bound excited electronic state above the threshold to dissociation. A “probe” pulse (blue arrow) arrives at set time-intervals after the pump pulse indicated by the pump-probe delay, τ , and ionizes one or more fragments. A “molecular movie” of the dissociation reaction can be generated by recording data at a series of τ .

the work presented in this thesis, the focus will be on nuclear dynamics. Femtosecond lasers opened up a whole new field, allowing chemists to follow molecular processes, reactions, and dynamics in real time, thus vastly improving our understanding of these processes.

1.2 Femtochemistry

The first femtosecond-resolved pump-probe measurement [25] was reported by Zewail and coworkers on the dissociation of ICN [7, 40, 41]. The “pump” pulse was used to excite ICN to an excited electronic state of repulsive character that generated I + CN photofragments. The molecule in its transition state, $\text{ICN}^\ddagger$, was ionized by a “probe” pulse at subsequent time intervals after the pump pulse. Thus, a series of quick snapshots of the evolving reaction lead to the first femtosecond “molecular movie” of

a photo-induced reaction [7, 40].

Zewail and coworkers also showed that NaI can be prepared at a variety of Na-I bond distances by pumping NaI from the ground electronic state to an excited electronic state, which are ionic (covalent) and covalent (ionic) in character, respectively, at small (large) internuclear distances. NaI* was then ionized with a probe pulse at a series of pump-probe delays corresponding to various Na-I bond distances along the reaction coordinate [9]. The authors observed resonance structures which were a direct result of the Na-I bond in the excited structure converting from covalent to ionic in character along the reaction coordinate [9]. In addition to probing the dynamics of a photo-induced reaction, femtosecond pulses were used to control the outcome of photo-induced reactions such as XeI + I [42]. Zewail’s work opened up a whole new field, called femtochemistry, which was acknowledged with the award of the Nobel Prize in Chemistry in 1999 [32].

More complex molecules have since been investigated using femtosecond-resolved pump-probe measurements. Bañares and coworkers studied the femtosecond-resolved photodissociation of CH₃I between 190-280 nm. They probed in “real-time” the photodissociation of CH₃I *via* the first absorption band, the *A*-band, which proceeded through non-adiabatic curve crossing [43]. Corrales *et al.* observed in ‘real-time’ that the photodissociation *via* the next absorption band, *B*-band, proceeds mainly through a Herzberg Type I or *electronic* predissociation [44]. The CH₃ fragments in this particular experiment were ionised using a (2+1) REMPI scheme, in which two photons around 330 nm are used to excite the molecule to a resonant excited state and a third photon promotes the molecule over the ionization threshold.

Various other probe schemes have been used in pump-probe experiments, for example: laser-induced fluorescence [7, 8], multi-photon ionization [40], time-of-flight mass spectrometry [30], transient absorption [45], and Coulomb explosion imaging (CEI) [46–51]. In the femtosecond work presented in this thesis, molecules were ionized using the Coulomb explosion imaging technique, details of which are discussed in the following section.

1.3 Coulomb Explosion Imaging

In Coulomb explosion imaging (CEI) [46–62], multiple electrons are removed from a target molecule to generate a highly charged, unstable molecular ion. The repulsive forces between the charged sites lead to the Coulomb explosion of the molecular ion, during which multiple charged fragments may be generated. Further details on the principles of CEI are given in Chapter 4. The emission direction of ions can reflect the direction of the bond axis that the ions originate from at the moment of initial ionization [63, 64]. This is called the “axial recoil approximation”. Deviations from this approximation have been observed in molecules larger than a diatom, which may be due to vibrations and bending of the molecule [60, 65, 66]. Stapelfeldt and coworkers [60] developed a method to deconvolute nonaxial effects from their data sets by investigating the correlations between the emission directions of the ions.

In all the CEI work mentioned so far, an intense 800 nm near-IR (NIR) pulse was used to induce a Coulomb explosion in the target molecule through strong-field ionization [51, 54, 56–62, 67–73]. In strong-field ionization, the laser field ($>10^{14}$ W cm $^{-2}$) is so strong that it deforms the Coulomb potential to such an extent that the potential barrier to ionization is significantly reduced and an electron can be removed from the system with greater ease. Coulomb explosion in a molecule may also be induced through inner-shell ionization [62, 74–85]. A photon of high energy in the extreme ultraviolet (XUV) or X-ray regime can eject an electron from a core orbital. The core vacancy is filled by a fast Auger process [86–88] that leads to the ejection of at least one other electron from the valence states. The multiply charged molecular ion can subsequently Coulomb explode to generate several charged fragment ions [77, 81–83]. In this thesis, the Coulomb explosion of 2,6-difluoriodobenzene is probed by NIR strong-field ionization and XUV inner-shell ionization to investigate the validity of the axial recoil approximation, as discussed in Chapter 7.

Structural information on a biphenyl molecule was extracted by several authors using CEI [54, 56–59, 61, 73]. Christensen *et al.* demonstrated the coherent control of torsional motion in a biphenyl molecule using two intense, femtosecond nonresonant “kick” pulses followed by strong-field ionization with an intense 800 nm femtosecond

pulse [57]. Femtosecond-resolved pump-probe CEI experiments were carried out by Erk *et al.* and Boll *et al.* on the photodissociation of CH_3I using either 800 nm or 267 nm pump pulses, and subsequent multi-photon inner-shell ionization by an X-ray pulse. Data at a series of pump-probe delays were recorded which revealed photodissociation and charge transfer dynamics in the molecule on the femtosecond timescale. Ibrahim *et al.* used a UV-pump and NIR-probe scheme to observe proton migration from the acetylene cation to the vinylidene cation using CEI [72].

In the experiments mentioned so far, a wide variety of detection systems were used to record the charged fragments generated by the probe pulse. These include: charged-coupled device (CCD) cameras [15–17, 21], delay-line anodes [72, 77], and time-stamping devices [54, 56–59, 61, 73]. Further details of these particle detectors are given in the following section.

1.4 Particle Detectors

The choice of a particle detector is very much based on factors such as: count-rate, repetition rate, the number of mass-to-charge fragments, the spatial and temporal resolution, as well as data handling and read-out times of the data generated. No one detector is a perfect choice, but some are better suited than others for a particular type of experiment. This section highlights the advantages and disadvantages of several commonly used particle detectors.

In the experiments discussed so far, the method of velocity-map ion-imaging (VMI) was used to project charged particles onto a position- and time-sensitive detector. The most commonly employed imaging system in VMI measurements is a set of microchannel plates (MCPs) coupled to a phosphor screen and a charge coupled device (CCD) camera. When a charged particle impacts onto the MCPs, an avalanche of electrons is produced within the pores of the MCPs that amplify the particle signal by up to 10^6 times. When electrons impact on the phosphor screen, photons are emitted and then recorded by the CCD camera.

A CCD camera contains an array of pixels that are sensitive to light, and the pho-

tons that are incident on each pixel lead to the build-up of charge that is subsequently read-out. A single image is therefore recorded from the array of pixels in each acquisition cycle. To record a detector image for a specific mass-to-charge (m/q) fragment, the MCPs can be pulsed ‘on’ only during the arrival-time of the m/q of interest to minimise background contributions. While this is an efficient method, it is limited to one fragment ion per acquisition run due to the time-gating requirements, and images for different fragments have to be recorded separately. Delay-line anode and ‘intelligent’ pixel detectors have since been developed to overcome this time-gating restriction.

1.4.1 Anode-Based Detectors

Anode-based detectors are ideally suited for low count-rate conditions [89–99], they offer very good spatial and temporal resolution, and can be operated at very high repetition rates (>1 kHz).

Wedge and strip detectors (WSDs) [89, 100] were the first anode-based detector developed [89] and mounted behind the MCPs. In general, WSDs consist of three electrodes, as shown in Figure 1.5(a): the wedge (W), strip (S), and Z-electrodes (Z). Once the electron cloud, which is emitted from the back of the MCP, impacts onto the WSD, the build-up of charge is distributed between the three electrodes. The x - and y -coordinates of the particle impact can be calculated using

$$x = \frac{2Q_S}{Q_W + Q_S + Q_Z}, \quad (1.3)$$

$$y = \frac{2Q_W}{Q_W + Q_S + Q_Z}, \quad (1.4)$$

where Q_W , Q_S , and Q_Z are the charge signals collected by the wedge, anode and z-electrodes, respectively. WSDs have good spatial and time-resolutions down to $40\ \mu\text{m}$ and $6\ \text{ns}$, respectively [95]. However, the primary disadvantages of WSDs are their slow read-out rates and their inability to detect multiple events.

Delay-line anode (DLA) detectors [90–94] consist of one or more wound wires that have a constant voltage applied to them, and are mounted behind a pair of MCPs. Figure 1.5(b) shows a typical DLA detector with two separated delay lines wound

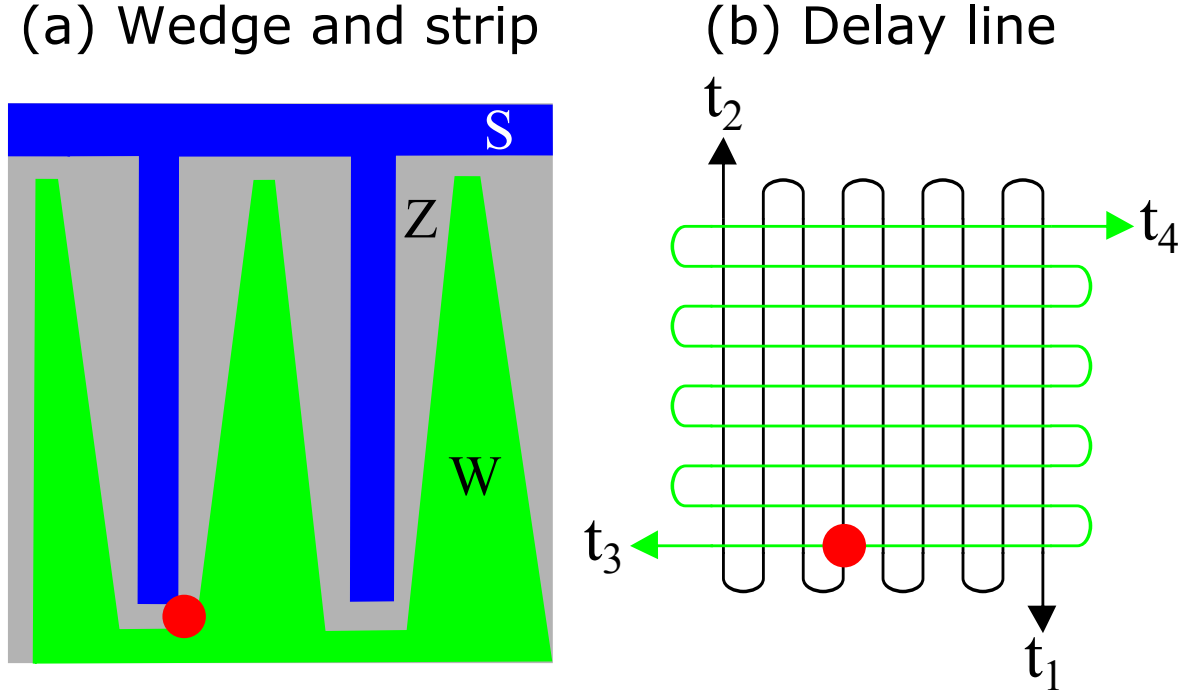


Figure 1.5: Schematic of two anode-based detectors: (a) A wedge and strip detector (WSD) and (b) a delay line anode (DLA) detector. In panel (a), the WSD consists of three electrodes which are the wedge, strip and z-electrodes. In panel (b), two wound delay line wires are placed orthogonal to one another. The impact of a particle on each detector is indicated by a red circle.

orthogonal to each other. The electron cloud from the back of the MCP impacts onto the delay line wires and consequently leads to a small reduction in the voltage on each wire. Thus, two signals are generated, one on each delay line wire. The two signals travel in both directions towards the end of the wires. The difference in the propagation times, t_1 to t_4 , on both wires are used to calculate the spatial positions x and y , as given by

$$x = k(t_1 - t_2), \quad (1.5)$$

$$y = k(t_3 - t_4), \quad (1.6)$$

where k is a proportionality constant, t_1 and t_2 are the time at which the first signal reaches the beginning and the end of the first wire, respectively, while the times at which the second signal reaches the beginning and the end of the second wire are given by t_3 and t_4 , respectively. The arrival-time of the event, t , is determined as

$$t = \frac{t_1 + t_2 + t_3 + t_4}{4}. \quad (1.7)$$

Delay-line anodes (DLAs) can record the position and arrival-time of an event with a precision of $100\ \mu\text{m}$ and $100\ \text{ps}$, respectively [91–94]. In the simplest DLA detector, only one particle can be detected across the whole surface at any given time. Any particle impact that occurs in the following $100\ \text{ns}$ period is not detected, and is referred to as the “dead time”. Several particles can be simultaneously detected using variations of DLA detectors. In one example, three delay lines arranged in a hexagonal geometry, referred to as a hexanode DLA detector, have been reported to detect tens of ions with the same mass-to-charge ratio in one acquisition shot [96, 99]. In general, however, the limited multi-hit capability of anode-based detectors is not sufficient enough to be used in 3D and multi-mass imaging experiments that are typically operated at high count-rates (*i.e.* >100 ions per shot) at $10\ \text{Hz}$ repetition rate. In 3D imaging, the full Newton sphere of ions is capture by recording the full three-dimensional velocity distribution of ions. In multi-mass imaging, multiple mass-to-charge fragments are recorded within the same acquisition cycle. Further details of these types of experiments are given in Chapter 3.

1.4.2 ‘Intelligent’ Pixel Detectors

The storage of timing information on each pixel lead to the development of ‘intelligent’ pixel detectors [62, 101–114]. These detectors solve the multi-hit problem under high count-rate conditions using two general approaches, namely: fast-framing CCD cameras and event-triggered complementary metal-oxide semiconductor (CMOS) sensors. Fast-framing CCD cameras can acquire multiple frames in a single acquisition window with nanosecond time-resolution [101–103, 108]. However, these cameras suffer from data handling issues due to the acquisition of complete image frames in each acquisition cycle that quickly generate vast amounts of data which consist mostly of zeros, as most pixels have not been triggered ‘on’.

A more efficient approach is to use event-based pixel detectors such as the Pixel Imaging Mass Spectrometry (PImMS) [109–111, 113–116] and TimePix [104, 106, 107] sensors. These sensors consist of an array of independent pixels that contain one or more timing counters in each pixel, which can store the arrival-time of an event as a

‘time-stamp’ with a precision of ~ 10 ns if its intensity exceeds a user-defined threshold [104, 106, 107, 109–111, 113]. Once the acquisition cycle is completed, the arrival-times and positions of the detected particles are transferred to a computer and stored in a file.

The TimePix sensor [104, 106, 107] has successfully demonstrated its 3D imaging capability [107] using a composite sensor based on four ‘sub-sensors’ that yield an effective size of 512×512 pixels. The TimePix sensors can be operated in three modes: Medipix, Time-over-Threshold (ToT), and Time-of-Arrival (ToA) modes. Medipix mode is used to count the total number of particles detected in each acquisition cycle. In ToT mode, the width of the signal pulse generated within the pixel can be measured and can be related to the energy of the particle. In ToA mode, the arrival-time time of the particle is recorded. A camera-based system has been developed by Nomerotski and coworkers that uses the TimePix sensor (TimepixCam) to time-stamp events using one digital counter with a 15 ns timing precision [117–119]. Since only one counter is available to store timing information in each pixel, this can lead to the non-detection of ions that arrive at a pixel that has already recorded a signal [113]. The next generation of the TimePix sensor, TimePix3 [120], overcomes this issue by reading out each ion signal to a file as soon as it has been detected before resetting the pixel to record subsequent signals in the same acquisition cycle. Although TimePix3 can record the arrival-times of events with 1.56 ns timing precision, it does feature a significant “dead time” of 475 ns [120]. Work on the successor to the TimePix3 sensor, TimePix4, has begun. This sensor will also consist of a composite sensor made of four individual sensors with an overall sensor size of 512×512 pixels but with a significantly lower timing precision of approximately 200 ps.

The PImMS sensor also consists of an array of independent pixels, each containing four timing counters that can time-stamp an event with a 12.5 ns precision and a dead time of ~ 100 ns [109–111, 113, 115, 116]. Like TimepixCam, it is employed within a camera-based system that is typically placed behind a phosphor screen detector set-up to record flashes of light which correspond to the detection of ion events [109–111, 113, 115, 116]. Two generations of the PImMS camera currently exist, PImMS1 and

PImMS2, which are differentiated by their total pixel array size (PImMS1: 72×72 pixels; PImMS2: 324×324 pixels). Further details of the PImMS camera are given in Chapter 2.

Detectors with multi-hit capabilities, such as hexanode and time-stamping detectors, can be used to record multiple correlated mass-to-charge fragments in a single acquisition cycle. This provides an opportunity to unravel structural information on the parent molecule, and to identify the fragmentation pathways through which certain fragments are generated. These correlations can be obtained through either the coincidence or covariance methods; the former is a direct counting method and the latter is a statistical method.

1.5 Coincidence and Covariance Imaging

The correlation between two or more variables can be determined through coincidence or covariance analyses, depending on the experimental conditions such as the count rate. Coincidence analysis [121, 122] is a direct counting method, where the detection of two or more correlated variables is carried out at very low count rate conditions (*i.e.* $\ll 1$ counts per shot). In ion imaging experiments, the significance of keeping the count rate very low is that the detection of two ion fragments must originate from the same molecule. Covariance analysis [54, 56–59, 61, 122–124] is a statistical method, which calculates the average number of times two or more correlated variables were detected in each acquisition shot [122, 124], and can be operated at high count rate conditions (*i.e.* $\gg 1$ counts per shot).

1.5.1 Coincidence Analysis

The coincidence between two variables X and Y is described by [122]

$$Coinc(X, Y) = \sum_{i=1}^{i=N} X_i Y_i, \quad (1.8)$$

where N is the total number of laser shots, and i is the laser shot number. Walter Bothe developed the method of coincidence spectroscopy, for which he received the Nobel Prize in Physics in 1954 [121]. It was not until 1984 that two coincident charged fragments were detected from the same molecule, utilizing the photoion-photoion-coincidence (PIPICO) method developed by Dujardin *et al.* [125]. However, the PIPICO method only provides the ToF difference between the coincident photoions, and so is not suitable for complex systems since the same ToF difference could be detected for different pairs of coincident ions. In the photoelectron-photoion-photoion (PEPIPICO) method employed by Eland *et al.* [126] and Frasninski *et al.* [127], the photoelectron signal was used as a marker for the start time (t_0) of the ionization process which enabled the absolute ToF of the two coincident photoions to be determined. PEPIPICO therefore leads to the unambiguous identification of the ion pairs.

In general, the method of coincidence has been widely used to unravel the dissociation and reactivity of multiply charged molecules [128]. A large number of small molecular dications have been shown to be metastable, which can consequently live long enough to be able to interact with atoms, molecules and photons [129]. Stephen Price [130] showed that molecular dications, such as CF_3^{2+} and CF_2^{2+} , were able to undergo chemical reactions following collisions with neutral species. A femtosecond-resolved study by Bañares and coworkers [131] also observed this metastable character in CH_3I^{2+} dications. The dication was present in the ToF spectrum, which was on the order of microseconds. The methyl fragments also had two distinct KER channels, and comparison to *ab initio* calculations of the potential energy curves involved showed that the excited electronic states of CH_3I^{2+} were metastable [131]. Légaré *et al.* studied in “real time” the complex dissociation dynamics of SO_2^{3+} molecular ions using the triple coincidence method in the femtosecond-resolved pump-probe of SO_2 [132].

In a five-fold coincidence study by Gagnon *et al.* [66], the molecular structure of CH_2Cl_2 was completely reconstructed by relating the velocities of the five fragments. Pitzer *et al.* [71] also used the five-fold coincidence method to determine the absolute molecular stereochemistry in CHBrClF by CEI.

Measurements that employ the coincidence analysis require the strict condition that

the count rate must be less than one count per acquisition shot. In the case when the count rate is higher (*i.e.* $\gg 1$ count per shot), falsely correlated signals (called ‘false coincidences’) will be detected. However, the appearance of false coincidences (at high count rate conditions) can be corrected for by covariance analysis, details of which are given in the following section.

1.5.2 Covariance Analysis

In gas-phase spectroscopy experiments, Frasinski *et al.* [123] discovered that the fluctuations in the ToF of two particles of interest were correlated with the fluctuations in the laser pulse; *i.e.* a rise (fall) in the pulse intensity lead to a rise (fall) in the ToF intensity of the particles. Since ion imaging experiments on dilute gas-phase samples follow Poisson statistics, the mean of each ion distribution is equal to its variance. As a result, the mean (variance) of detecting two uncorrelated ions, $\langle X \rangle \langle Y \rangle$, can be subtracted away from the mean (variance) of detecting two correlated fragment ions, $\langle XY \rangle$, to generate a covariance map, $Cov(X, Y)$ [123]. The covariance between two variables is described by [54, 122–124]

$$Cov(X, Y) = \langle XY \rangle - \langle X \rangle \langle Y \rangle, \quad (1.9)$$

where $\langle X \rangle$ is the average number of counts measured for particle X as given by [54, 122–124]

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

and $\langle XY \rangle$ is the average number of counts measured for particles X and Y detected in coincidence with each other as described by [54, 122–124]

$$\langle XY \rangle = \frac{1}{N} \sum_{i=1}^{i=N} X_i Y_i. \quad (1.11)$$

In the limit of very low count rate conditions (*i.e.* $\ll 1$ count per shot), the contribution from the uncorrelated coincidence term in the $Cov(X, Y)$ becomes negligible (*i.e.* $\langle X \rangle \langle Y \rangle \sim 0$) and so $Cov(X, Y)$ is directly related to the correlated coincidence

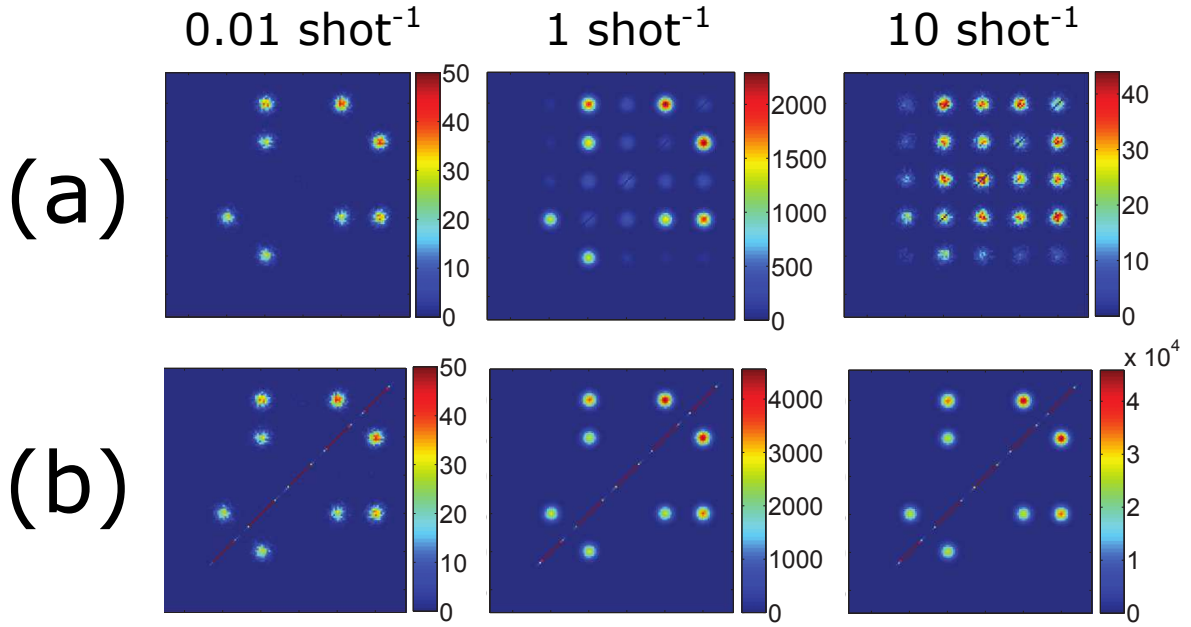


Figure 1.6: The two-fold (a) coincidence and (b) covariance maps at three count rate conditions: 0.01, 1, and 10 counts shot^{-1} . This figure was adapted from Reference [122].

term, $\langle XY \rangle$ [122] through [122, 124]

$$\text{Coinc}(X, Y) = N \text{Cov}(X, Y). \quad (1.12)$$

Figure 1.6 shows simulated coincidence (top row) and covariance (bottom row) maps corresponding to particles X and Y at three different count rate conditions of: 0.01 (left), 1 (middle) and 10 (right) counts per shot [122]. Here, the $\text{Coinc}(X, Y)$ and $\text{Cov}(X, Y)$ maps are equivalent at the very low count rate of 0.01 counts per shot when ignoring the diagonal line in the latter map. This diagonal line corresponds to a autovariance signal where two of the same particles are in covariance with each other. As the count rate increases to 1 count per shot (middle panel), falsely correlated signal between the two particles appear in the coincidence map (top row), whilst no such falsely correlated signal is present in the $\text{Cov}(X, Y)$ map. This is because the covariance analysis method takes into account contributions from uncorrelated signal, $\langle X \rangle \langle Y \rangle$. In the covariance maps, an increase in the count rate to 10 counts per shot (right panel) leads to improved signal:noise without the appearance of false coincidences. Whilst in the corresponding coincidence map, even more falsely correlated signals appear.

The covariance mapping method has been used to study the fragmentation of small molecules [123, 133–136], as well as multi-photon processes initiated by intense X-ray pulses using a free-electron laser [137]. Larger molecules have also been studied through covariance analysis, which include: acetylene and ethane [138], fullerenes [139], and biphenyl molecules [54–61, 140]. Berrah *et al.* [139] observed bond breaking and bond making processes using covariance analysis following radiation damage of fullerenes. Hansen *et al.* [140] and Christensen *et al.* [57] monitored torsional motion in a biphenyl molecule in ‘real-time’ by tracking the dihedral angle in the molecule. Slater *et al.* [54, 56, 58] demonstrated the multi-mass imaging capability of the PImMS camera in recording angular covariances between two recoil ions with different mass-to-charge fragments, which revealed significant structural information on the biphenyl molecular prior to its Coulomb explosion. Pickering *et al.* [61, 73] extended the angular covariance analysis to three recoil ions, which was subsequently used to distinguish between the *R* and *S*-enantiomers of the biphenyl molecule. Christiansen *et al.* also studied the Coulomb explosion of 1,4-diiodobenzene molecules that were either isolated or embedded in helium nanodroplets, and they observed, using covariance analysis, that the helium environment did not alter the angular correlations between fragments [141].

1.6 Outline of Thesis

The work presented in this thesis primarily focuses on the application of fast imaging sensors, PImMS1 and PImMS2, to the investigation of 3D imaging, Coulomb explosion imaging, and femtosecond-resolved dynamical experiments. Chapter 3 presents the 3D imaging capabilities of the PImMS camera in capturing the full 3D velocity distribution of CO^+ and S^+ ions following the one-colour photodissociation of OCS.

Chapter 4 provides detailed insights into the principles of Coulomb explosion imaging (CEI), the ionization schemes used to induce the Coulomb explosion of a molecule as well as the approaches used to control the alignment and orientation of molecules with either or both laser and electric fields.

Chapter 5 uses CEI and covariance analyses to identify the structures of four diflu-

oriodobenzene and two dihydroxybromobenzene isomers. Covariance analysis is also used to identify the structural isomers present in a mixture measurement containing two difluoriodobenzene isomers. The covariance analysis is extended to Chapter 6, where the *trans-cis* isomerization of 4,4'-difluoroazobenzene (DFAB) is investigated in 'real-time' through femtosecond-resolved pump-probe measurements that monitor the evolution of *trans*-DFAB to *cis*-DFAB.

In Chapter 7, the laser-induced adiabatic alignment and mixed-field orientation of 2,6-difluoriodobenzene molecules are probed by CEI following either near-infrared strong-field ionization or extreme-ultraviolet multi-photon inner-shell ionization using free-electron laser pulses. Chapter 8 investigates the photodissociation and charge transfer dynamics of laser-aligned methyl iodide and 2,6-difluoriodobenzene molecules in 'real-time' using ultraviolet-laser pump and extreme-ultraviolet FEL probe pulses. A brief summary of the work presented in this thesis as well as an outlook on possible future work is given in Chapter 9.

In the following chapter, details of the experimental principles and set-ups used in this work are outlined.

Chapter 2

Experimental Principles and Apparatus

This chapter presents a detailed description of the experimental principles and equipments used in this thesis, which were carried out in three separate laboratories, those of: Prof. Mark Brouard at the University of Oxford, Prof. Henrik Stapelfeldt at the University of Aarhus, and Prof. Daniel Rolles at the Free-electron LASer facility in Hamburg (FLASH), DESY.

The three experimental set-ups share several common features: a molecular beam, pulsed lasers, velocity-map ion-imaging (VMI) electrostatic plate assembly, position- and time-sensitive imaging detectors, and a camera. Firstly, molecules supersonically expanded in a molecular beam were aligned, oriented, pumped and/or probed with nanosecond and/or femtosecond laser pulses. In all measurements, a probe pulse was used to generate charged ion fragments. The trajectories of the resulting charged fragments were manipulated to map the initial three-dimensional (3D) velocity distribution onto a position- and time-sensitive detector using VMI. Central to the work presented here was the application of the Pixel Imaging Mass Spectrometry (PIImMS) camera in capturing both the position and arrival-time of all mass-to-charge fragments simultaneously, under the same experimental conditions.

The work presented in this thesis was carried out at relatively high count rates

under two VMI modes: 3D imaging and multi-mass crushed imaging. In the former, the full 3D velocity distribution of a particular mass-to-charge fragment was directly recorded with the PImMS camera. In the latter, the 3D velocity distribution was ‘pancaked’ onto the detector to record a crushed two-dimensional (2D) velocity distribution for all mass-to-charge fragments. Two generations of the PImMS camera were used (PImMS1: 72×72 pixels; PImMS2: 324×324 pixels). This chapter is organised around the various experimental principles and apparatus that were used in this thesis; a brief overview of each experimental apparatus is given.

2.1 Overview

The Oxford VMI Spectrometer

The Oxford spectrometer was employed in the 3D imaging measurements presented in Chapter 3. The spectrometer, shown in Figure 2.1, consists of three chambers: the source chamber, the reaction chamber, and the detection chamber. A gas mixture consisting of the target molecule seeded in a noble gas was generated in an external stainless steel sample bottle fitted with a two-stage regulator at a backing pressure of 1.5 bar. A small roughing pump (Leybold D4B), with a halogen filter installed, was connected to the sample reservoir to avoid corrosion by pumping on the line whenever the experiment was not in use. The gas mixture was supersonically expanded into the source chamber through the nozzle of a pulsed (10 Hz) General Valve (Series 9).

The resulting molecular beam was collimated using a skimmer (1 mm diameter, Beamdynamics Inc.) located between the source and the reaction chamber. In the reaction chamber, the collimated beam enters a set of DC sliced imaging electrostatic plates [142] through a 0.9 mm aperture in the first plate. The ion optic assembly consists of four electrostatic plates, with voltages applied to the first three plates whilst keeping the last plate electrically grounded. The collimated beam was crossed orthogonally in the interaction region, between the first two electrostatic plates, by a laser pulse with an electric field, ϵ , as shown in Figure 2.1.

The laser pulse entered and exited the reaction chamber through UV-grade fused

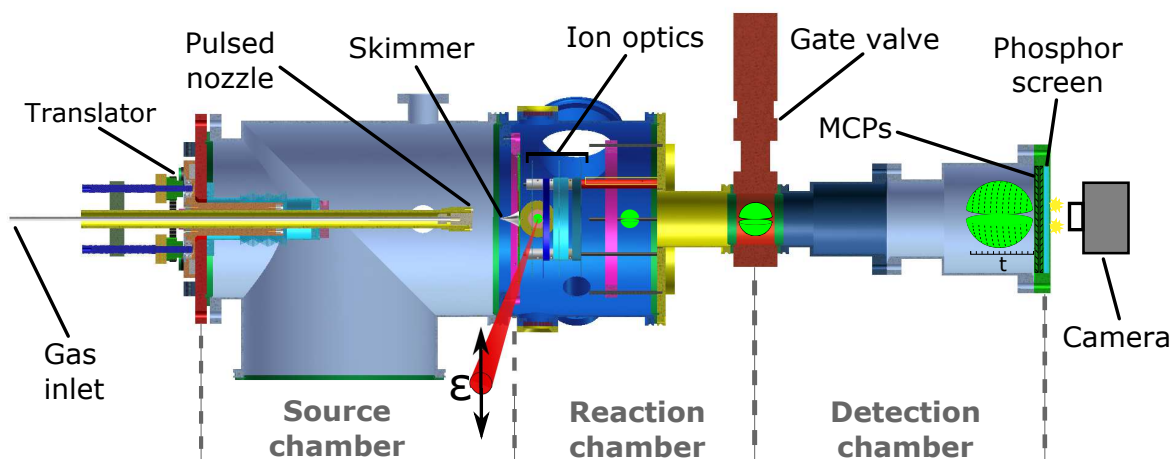


Figure 2.1: A side-on two-dimensional model of the Oxford VMI spectrometer. The principal components are identified and labelled. See text for details.

silica windows (40 mm diameter $\times$ 4 mm thickness, Crystran Ltd). The reaction chamber was separated from the detection chamber by a gate valve, as shown in Figure 2.1. The detection chamber consists of the time-of-flight (ToF) tube and a position- and time-sensitive detector. A double-layered, cylindrical μ -metal magnetic shield was installed in the flight tube to protect against stray magnetic fields that could adversely perturb the trajectories of charged particles. In the detection chamber, a position- and time-sensitive detector is composed of two microchannel plates (MCPs) and a P47 phosphor screen (PS). Once the charged particles impact onto the detector, flashes of light are emitted from the back of the phosphor screen which are captured by either a conventional charged-coupled device (CCD) camera, the PImMS1 or the PImMS2 camera.

The source chamber had a typical pressure of 2×10^{-7} Torr, and was pumped by a 600 ls^{-1} turbomolecular pump (Leybold TMP600), backed by a rotary pump (Leybold, Trivac D40V). The reaction and detection chambers had a typical pressure of 2×10^{-8} Torr, and were differentially pumped by 300 ls^{-1} and approximately 50 ls^{-1} turbomolecular pumps (Alcatel ATP 400 and Pfeiffer Vacuum TMU 071P, respectively) backed by a single rotary pump (Leybold, Trivac D40V).

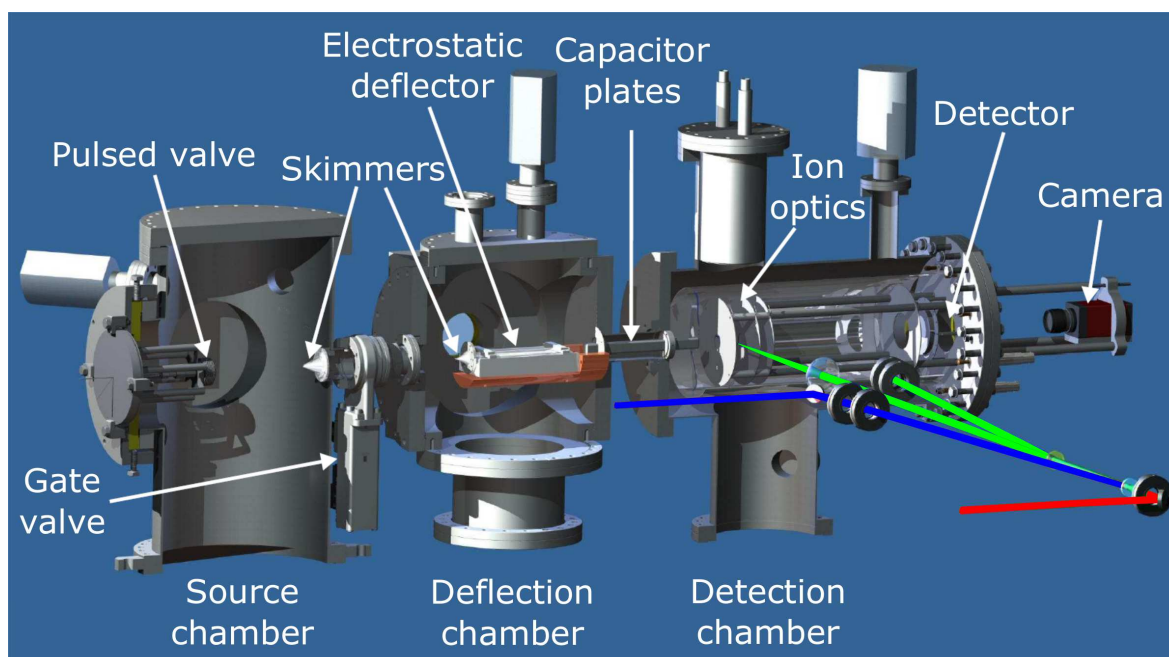


Figure 2.2: A schematic of the Aarhus VMI spectrometer with the three chambers and all the parts of the set-up labelled. In the alignment measurements discussed in Chapter 5, a 1064 nm YAG pulse (green beam) and an 800 nm probe pulse (red beam) were used. In the time-resolved pump-probe measurement discussed in Chapter 6, a 330 nm pump pulse (blue beam) and an 800 nm probe pulse (red beam) were used. See text for details. This figure was adapted from Reference [145].

The Aarhus VMI Spectrometer

The Aarhus spectrometer was employed in the work presented in Chapters 5 and 6. The spectrometer consists of three chambers, as shown in Figure 2.2, which are: the source chamber, the deflection chamber, and the detection chamber. In the source chamber, the target gas molecule was seeded at a high pressure (80 bar) in helium and supersonically expanded into the source chamber through an Even-Lavie pulsed valve (E.L.-7-4-2005-HRR) [143, 144]. The source and deflection chambers are separated by a skimmer with a 3 mm orifice (Beam Dynamics Inc, Model 50.8) and a gate valve. The molecular beam was collimated as it passed through a second skimmer (1 mm, Beam Dynamics Inc, Model 2) that was positioned in front of the 15 cm long electrostatic deflector. The deflector was not utilized in the measurements presented in Chapters 5 and 6, and so the molecular beam passed through undeflected.

In the detection chamber, the molecular beam entered the ion optic assembly consisting of three electrostatic plates. The electrostatic plates were surrounded by μ -metal shielding to protect against stray fields. The molecular beam was intersected by one

or more pulsed lasers between the repeller and extractor plates. The charged particles generated by the probe pulse were accelerated towards a position- and time-sensitive detector using electric fields created with the ion optics using the method of VMI. The detector consists of two MCPs and a P47 phosphor screen. Flashes of light emitted from the phosphor screen were captured by either the PImMS1 or the PImMS2 camera.

The FLASH VMI Spectrometer

The application of the free-electron laser at Hamburg (FLASH) was central to the free-electron laser (FEL) related work presented in Chapters 7 and 8. Free-electron lasers provide access to high photon energies (> 60 eV) in the multi-photon regime ($10^{12} - 10^{13}$ photons per pulse) with ultrashort (50 - 300 fs) pulses. Further details on the operating principle of an FEL and other high photon energy sources are given in Chapter 4. The permanent CFEL-ASG Multi-Purpose (CAMP) experimental endstation [146] was used at Beamline 3 (BL3), consisting of the source chamber, the deflector chamber and the reaction chamber, as illustrated in Figure 2.3.

In the source chamber, a pulsed molecular beam of target gas molecules seeded in neon was generated using a pulsed Even-Lavie valve. The molecular beam was collimated with a skimmer (2 mm, Beamdynamics Inc.) before entering an electrostatic deflector. The deflector, which is based on the design by Chamberlain *et al.* [147], was used to both separate the target molecule from the carrier gas, and to select the rotationally coldest part of the beam to achieve the best degree of spatial confinement of molecules [148–151].

The deflected beam was skimmed for a second time (4 mm, Beamdynamics Inc.) before it was orthogonally crossed with up to three lasers in the centre of a double-sided VMI spectrometer [152]: a neodymium-doped yttrium aluminium garnet (YAG) laser, a titanium-sapphire (Ti:Sa) laser, and the FLASH free-electron laser. In Chapters 7 and 8, the target molecule was adiabatically aligned [148, 149, 152–160] using a nanosecond Nd:YAG laser. In a small set of measurements discussed in Chapter 7, the target molecule was also both aligned and oriented in space using mixed-field orientation [148, 150]. In Chapter 7, molecules were probed with either of the following

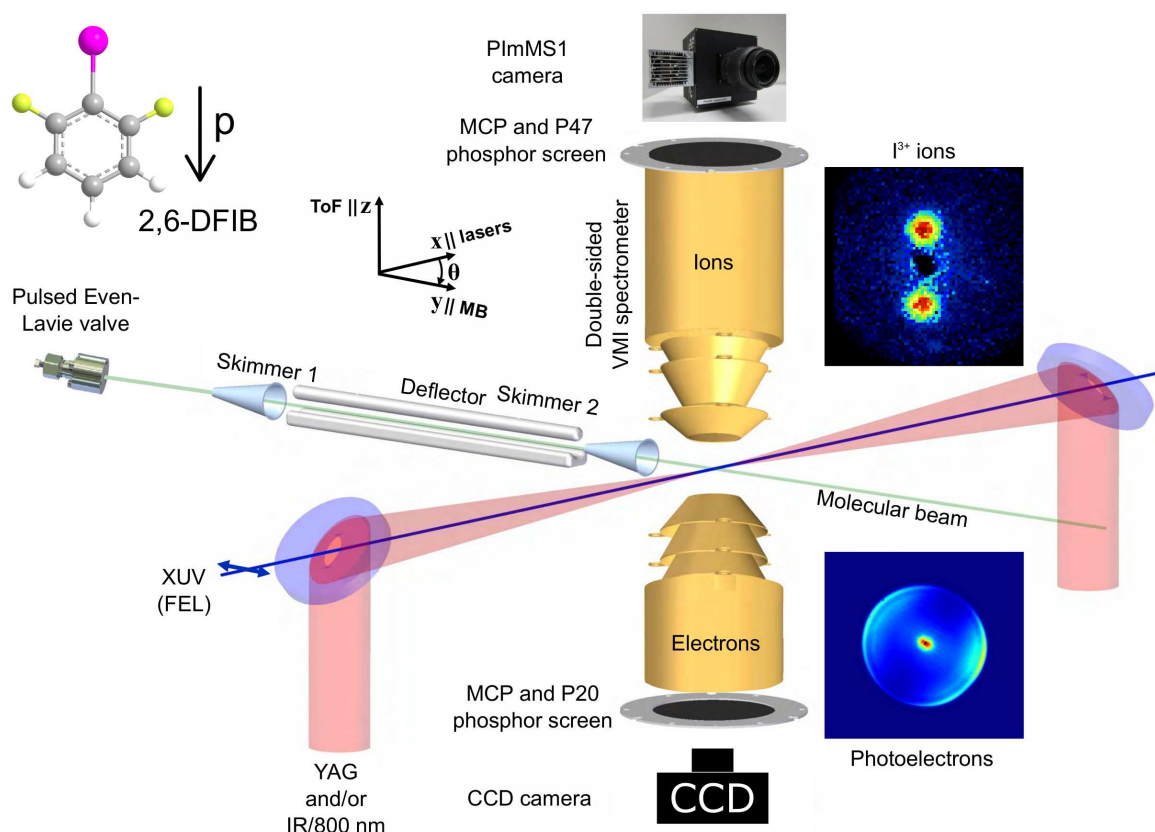


Figure 2.3: A side-on two-dimensional model of the CAMP endstation used in the FLASH experiments. The principal components are identified and labelled. The I^{3+} ion image (top) and the corresponding photoelectron image for 1D-aligned DFIB molecules is shown following ionization with an 11.6 nm pulse. On the left of the figure, the structure of the 2,6-DFIB molecule is presented, with the black arrow showing the direction of the molecules electric dipole moment. This figure was adapted from Reference [152].

two pulses: a high-intensity, femtosecond near-IR (NIR) pulse (800 nm; fundamental output of in-house FLASH Ti:Sa laser system) or an ultrabright, femtosecond extreme-ultraviolet (XUV) pulse (11.6 nm; FEL tuned to 11.6 nm). In the FLASH-related femtosecond-resolved measurements discussed in Chapter 8, the target molecule was photodissociated with an ultraviolet (UV) pulse (267 nm; frequency tripled-output of Ti:Sa) and probed with an extreme-ultraviolet (XUV) pulse (FEL tuned to 11.6 nm).

The charged ions (electrons) were velocity-mapped upwards (downwards) onto a detector. The ion detector consisted of a pair of MCPs and a P47 phosphor screen, while a pair of MCPs and a P20 phosphor screen were used for electron detection. Flashes of light were emitted from the detector as the avalanche of electrons impinged onto the phosphor screen. Either a conventional CCD or the PImMS1 camera captured the flashes of light from the ion side, while on the electron side, a (second) conven-

tional CCD camera was used. Although electron data was recorded during the FLASH beamtimes, they are not investigated in this thesis. High-resolution cation ToF spectra were also recorded simultaneously from the direct readout of the decoupled analog MCP signal using a high-resolution high-speed digitizer (Acqiris U1065A).

In the following sub-sections, details on the principles of the commonly used apparatus and methods are given.

2.2 Molecular Beam Sources

A molecular beam was generated by supersonic expansion of a gas sample from a container of high pressure ($p_1 \geq 1$ bar) through a small orifice, called a nozzle, and into an evacuated chamber of low pressure ($p_2 \leq 10^{-5}$ mbar). If the mean free path (λ_0), the average distance travelled by a moving particle between collisions, was much larger than the diameter of the orifice (d_o), then very few particles would collide with each other or leave the container (*i.e.* $\lambda_0 > d_o$) [161, 162].

An increase in the orifice diameter or the container pressure, p_1 , will lead to $\lambda_0 < d_o$ which has two consequences [161, 162]. Firstly, many more collisions between the gas particles will occur in the container, leading to the adiabatic cooling of (and energy transfer between) the colliding particles [161, 162]. Secondly, many more particles will escape into the evacuated chamber through an adiabatic, isentropic expansion, described by [161]

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{(\gamma-1)/\gamma} \quad (2.1)$$

where T_2 and p_2 are the final temperature and pressure, and T_1 and p_1 are the initial temperature and pressure. The heat capacity ratio, γ , is the ratio between the heat capacity at constant pressure, C_p , and the heat capacity at constant volume, C_v .

Since in a supersonic expansion $p_2 \ll p_1$ it follows then from Equation (2.1) that the internal temperature after expansion will be significantly reduced. This leads to a decrease in the internal energy of molecules after expansion, given by the equation $U_2 = (3/2)k_B T_2$, where k_B is the Boltzmann constant. To conserve the total energy in the system, a decrease in the internal energy will lead to an increase in the translational

(kinetic) energy [161, 162]. This leads to a significantly narrower velocity distribution of molecules after the expansion (*i.e.* lower internal energy) but a relatively high mean longitudinal velocity [161, 162].

In the 3D imaging measurements presented in Chapter 3, a pulsed General Valve (Series 9) was operated at a 10 Hz repetition rate with a backing pressure of 1.5 bar which generated a molecular beam with a rotational temperature of T_{rot} around 25 K [163–165]. In the femtosecond measurements, a pulsed Even-Lavie valve produced a molecular beam with a rotational temperature of approximately 1 K [166] using a high backing pressure of the gas mixture (Aarhus: 80 bar; FLASH: 20 bar). Although this valve can be operated at a repetition rate of up to 1 kHz, it was operated at significantly lower rates in the measurements presented in this thesis. In the work presented in Chapter 5, the Even-Lavie was operated at 10 Hz, limited by the PImMS2 camera. While in Chapter 6, the valve was operated at 200 Hz, limited by the PImMS1 camera. In the FLASH measurements presented in Chapters 7 and 8, the valve was triggered at a repetition rate of 10 Hz, limited by the in-house pump Ti:Sa laser.

The Even-Lavie pulsed valve has a thermocouple and a resistive heater attached to it, which allows the inlet sample to be heated to temperatures between 30–250°C. In the work presented in this thesis, the Even-Lavie valve was heated to between 70°C and 120°C in both the Aarhus and FLASH measurements to increase the vapor pressure of the sample, in order to generate a sufficiently high concentration of molecules for the expansion.

2.3 Optical Systems

An overview of the optical systems that were employed in this thesis is given in the following section. In the 3D imaging measurements, a nanosecond laser system was used, while in the Aarhus and FLASH measurements both nanosecond and femtosecond pulses were used.

2.3.1 Oxford Measurements

A 230 nm nanosecond pulse ($\tau = 5\text{--}6$ ns (FWHM); $I_0 = 1 \times 10^9$ W cm⁻²) was generated by a tuneable dye laser (Sirah CSTR-G-24), pumped by a pulsed Nd:YAG laser (Continuum, Powerlite Precision II) at a repetition rate of 10 Hz. The third harmonic pulse energy of the Nd:YAG laser was approximately 300 mJ at full power, and was attenuated by varying the delay in time between the flashlamp and Q-switch of the Nd:YAG laser. A Coumarin 460 dye solution dissolved in methanol (Amplifier: 0.035 gl⁻¹; Oscillator: 0.2 gl⁻¹) produced a peak power output of approximately 60 mJ per pulse.

The 460 nm pulse was frequency doubled using a BBO type I crystal (SHG 220) and separated from the fundamental by a set of four Pellin-Broca prisms. A set of optical prisms transported the 230 nm pulse to an 18 cm focal length lens which focussed the pulse into the interaction region inside the reaction chamber, with beam width of approximately 20 μ m. A photoelastic modulator (Hinds Instruments PEM-100) was installed in the beamline to switch the laser polarization of the 230 nm pulse to lie either parallel or perpendicular to the plane of the detector on alternate laser shots. The images from each polarization were accumulated into separate data buffers, which allowed data from both polarizations to be recorded under essentially identical experimental conditions.

2.3.2 Aarhus Measurements

In the Aarhus measurements, two experiments were carried out using two different femtosecond laser systems. The first experiment was a static study into the pure isomers of difluoriodobenzene and dihydroxybromobenzene in Chapter 5. The second experiment was a time-resolved pump-probe study into the *trans-cis* isomerization of 4,4'-difluoroazobenzene in Chapter 6. The former used the Spitfire HPR femtosecond laser system, while the latter used the Spitfire ACE system. A schematic of the optical set-up used in the Aarhus measurements is presented in Figure 2.4.

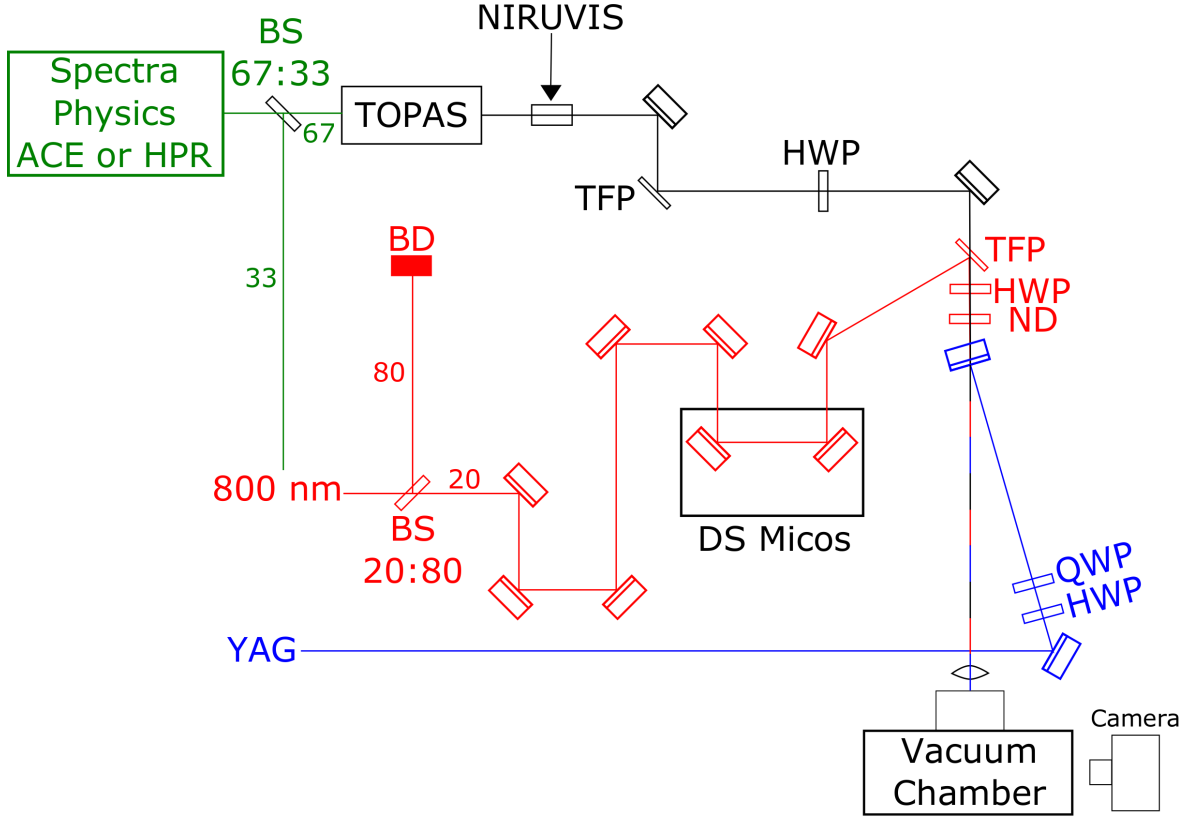


Figure 2.4: Optical set-up used in the Aarhus measurements for the 330 nm pump (black trace), 800 nm probe (red trace), and 1064 nm alignment (blue) pulses. The optics labels correspond to: BS (beam splitter), BD (beam dump), TFP (thin film polarizer), ND (neutral density filter), DS (delay stage), HWP (half-wave plate), QWP (quarter-wave plate). All unlabelled optics correspond to mirrors. Figure adapted from Reference [55].

A. Static Isomer Measurement

In the static isomer measurements presented in Chapter 5, two laser pulses were used: a 1064 nm adiabatic alignment pulse and an 800 nm probe pulse.

A 1064 nm adiabatic alignment pulse ($\tau = 10$ ns (FWHM); $I_0 = 8 \times 10^{11}$ W cm $^{-2}$) was generated using a Nd:YAG laser (Spectra-Physics, Quanta Ray Pro 270) at a repetition rate of 10 Hz, which had a measured pulse energy of around 230 mJ, and a measured beam width of $39 \mu\text{m} \times 36 \mu\text{m}$. The beam width is defined as the length it takes for the intensity to decrease from maximum to $1/e^2$ [55]. The peak intensity, I_0 , of a Gaussian laser pulse can be calculated using [55]

$$I_0 = \frac{4 \ln 2}{\pi^{3/2}} \frac{E_p}{\omega_0^2 \tau}, \quad (2.2)$$

where τ is the pulse duration (FWHM), E_p is the pulse energy, and ω_0 is the beam width of the focus [55]. A low enough peak intensity ($I_0 = 8 \times 10^{11} \text{ W cm}^{-2}$) was used to avoid strong-field ionization of the molecules by the alignment pulse whilst maximizing the degree of alignment. Either linearly or elliptically polarized light was used to induce one- or three-dimensional alignment of molecules, respectively, further details of which are given in Chapter 4. The YAG pulse was steered to the experiment through a series of mirrors. A half wave plate (HWP) and a quarter wave plate (QWP) were used to control the YAG polarization. The YAG pulse was focussed into the chamber with a $f = 300 \text{ mm}$ focusing lens, where f is the focal distance. The focal volume of the alignment pulse was approximately four times larger than that of the probe pulse.

An 800 nm probe pulse ($\tau = 30 \text{ fs}$ (FWHM); $I_0 = 3.0 \times 10^{14} \text{ W cm}^{-2}$) was generated by a Spectra-Physics Tsunami Ti:Sapphire oscillator ($\tau = 100 \text{ fs}$, 82 MHz repetition rate, $E_p = 10 \text{ nJ}$) pumped by a continuous wave Spectra-Physics Millennia V (Nd:YVO₄, 5 W, 532 nm). The output of the oscillator was then amplified to generate pulse energies of around 2.0 mJ ($\tau = 130 \text{ fs}$, 1 kHz repetition rate) using a Spectra-Physics Spitfire HPR regenerative chirped pulse amplifier that was pumped by a Spectra-Physics Evolution-30 Q-switched Nd:YLF laser (20 mJ pulses at 527 nm). The frequency spectrum of the laser pulse was broadened due to self-phase modulation [167] by passing the beam through an argon-filled capillary, utilizing the optical Kerr effect. The 800 nm laser pulses were then temporally compressed to approximately 30 fs using a prism compressor. A pulse energy of around 150 μJ and a beam width of $26 \mu\text{m} \times 32 \mu\text{m}$ were measured that gave a peak intensity of $3.0 \times 10^{14} \text{ W cm}^{-2}$.

B. Time-Resolved Isomerization Measurement

In the time-resolved pump-probe experiments presented in Chapter 6, two femtosecond laser pulses were used: a 330 nm pump pulse and an 800 nm probe pulse. The 5 W output of the Spectra-Physics Spitfire ACE-35F laser system was split with a 67% beamsplitter to generate two beam lines: the pump (3.4 W) and probe (1.6 W) pulses.

A 330 nm pump pulse ($\tau = 115 \text{ fs}$ (FWHM); $I_0 = 3 \times 10^{11} \text{ W cm}^{-2}$) was generated

from the output of a TOPAS optical parametric amplifier (OPA) which was pumped by the 800 nm output of the Spitfire ACE (3.4 W). The OPA was combined with a NIRUVIS extension which enabled the wavelength to be tuned to the ultraviolet-visible range. The pump pulse was then sent through a prism compressor to compress the pulse in time to approximately 115 fs. The beam passed through a telescope to control the beam width, with a measured focus of $31\text{ }\mu\text{m} \times 68\text{ }\mu\text{m}$, and was also used to overlap the two foci along the laser beam direction. The power was controlled using reflective neutral density filters that gave a measured pulse energy of $1.6\text{ }\mu\text{J}$ and a final intensity of $3 \times 10^{11}\text{ W cm}^{-2}$. The intensity of the pump pulse was weak enough to avoid strong-field ionization of the molecules. The polarization was linear and controlled by a HWP.

An 800 nm probe pulse ($\tau = 35\text{ fs}$ (FWHM); $I_0 = 2 \times 10^{14}\text{ W cm}^{-2}$) was generated using the remaining beam of the Spitfire ACE (1.6 W). The power of this pulse was reduced to 320 mW using a second beam splitter (20 % / 80 %). The probe pulse was then coupled onto a computer-controlled delay stage (Micos, LS-110) to adjust the time delay between the pump and the probe pulses by shortening or lengthening the distance that the probe pulse had to travel. After exiting the stage, the polarization of the probe pulse was controlled with a HWP, and the power was adjusted using a reflective neutral density filter that gave a final pulse energy of $67\text{ }\mu\text{J}$.

The probe pulse was overlapped spatially with the pump pulse using a 0° mirror and subsequently focused to $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ using a $f = 30\text{ cm}$ focusing lens into the chamber, which generated peak intensities of up to $2 \times 10^{14}\text{ W cm}^{-2}$. The cross correlation between the pump and probe pulses was measured using difference frequency mixing of the 800 nm and 330 nm pulses in a BBO crystal, which generated 568 nm light. The measured cross correlation was 120 fs (FWHM).

2.3.3 FLASH Measurements

In the static FLASH measurements presented in Chapter 7, a 1064 nm nanosecond alignment pulse was used with either the 800 nm or 11.6 nm femtosecond probe pulses. While in the time-dependent FLASH measurements discussed in Chapter 8, three pulses were used: a 1064 nm adiabatic alignment pulse, a 267 nm pump pulse, and a 11.6 nm

probe pulse.

A 1064 nm adiabatic alignment pulse ($\tau = 12$ ns (FWHM); $I_0 = 8 \times 10^{11}$ W cm $^{-2}$) was also generated using a Nd:YAG laser (Spectra Physics, Quanta Ray Pro 270-50) at a repetition rate of 10 Hz. It had a measured pulse energy of approximately 1.2 J, and a measured beam width of $80 \mu\text{m} \times 80 \mu\text{m}$. The intensity of the alignment pulse ($I_0 = 8 \times 10^{11}$ W cm $^{-2}$) was kept low enough in order to avoid strong-field ionization of the molecules.

The 800 nm pulse ($\tau = 70$ fs (FWHM); $I_0 = 2 \times 10^{14}$ W cm $^{-2}$) and 267 nm pulse ($\tau = 150$ fs (FWHM); $I_0 = 7 \times 10^{12}$ W cm $^{-2}$) were generated by the in-house Ti:sapphire (Ti:Sa) 10 Hz laser system at FLASH. The Ti:Sa oscillator pulses, which are synchronized to the master clock of the FEL, were amplified by a commercial chirped pulse amplifier (CPA) system (Hidra-25 Coherent) [168]. The resulting 800 nm pulse had a pulse energy of 120 μJ and a measured beam width of $20 \mu\text{m} \times 20 \mu\text{m}$, and a high peak intensity ($\sim 2 \times 10^{14}$ W cm $^{-2}$) was chosen to strong-field ionize the target molecules.

A 267 nm pulse ($\tau = 150 \pm 50$ fs (FWHM); $I_0 = 7 \times 10^{12}$ W cm $^{-2}$) was generated from the frequency-tripled output of the 800 nm beam, with a measured pulse energy of around 35 μJ . The 267 nm pulse was temporally compressed to approximately 150 ± 50 fs (FWHM) using a prism compressor, and subsequently focussed into the chamber using a telescope with a beam width of approximately $40 \mu\text{m} \times 40 \mu\text{m}$, giving a peak intensity of approximately 7×10^{12} W cm $^{-2}$. The peak intensity of the 267 nm pulse was also kept low to avoid strong-field ionization of molecules.

The pulses generated in the Ti:Sa laser hutch were transported under vacuum up to 20 m away to the experimental end-stations. The Ti:Sa beamline system was not directly connected to the experimental vacuum chambers, which provided a high degree of flexibility to, for example, adjust the beam size and focus of the optical pulse. The Ti:Sa laser pulse was propagated through the experimental chamber near-collinearly to the YAG alignment laser and the FEL, with all pulses polarized parallel to the plane of the detectors as shown in Figure 2.3. A delay stage was used to vary the delay in time between the Ti:Sa laser and the FEL pulses.

A. The FLASH Free-Electron Laser

The 11.6 nm femtosecond pulse ($\tau = 100$ fs (FWHM); $I_0 = 3 \times 10^{13}$ W cm $^{-2}$) was generated by the FLASH free-electron laser (FEL). Free-electron lasers (FELs) are accelerator-based lightsources that generate intense, femtosecond extreme-ultraviolet (XUV) and X-ray pulses ($10^{12} - 10^{13}$ photons per pulse, $\tau = 50$ -300 fs). Details of the operating principle of FELs is given in Chapter 4. The FLASH FEL was operated at an electron energy of 0.6 GeV in single-bunch mode (10 Hz repetition rate) with 180 pC bunch charge. XUV pulses were generated with a central wavelength of 11.6 nm (107 eV), a bandwidth of 2 eV (FWHM), and an average pulse energy of 32 ± 8 μ J. The FEL pulses had a typical pulse duration of ~ 100 fs (FWHM). This was determined from the measurement of the electron bunch duration that was recorded simultaneously with the FEL data presented in this thesis. The XUV pulse was transported to the experimental end-station and focussed into the chamber to a spot size of ~ 20 μ m in Beamline 3 (BL3) which generated a peak intensity of approximately 3×10^{13} W cm $^{-2}$.

B. The FLASH Diagnostics System

The FEL is a relatively unstable lightsource when compared to the optical laser, with no two FEL pulses being the same. As a result, the timing and synchronization between the FEL and optical pulses can temporarily drift. Therefore, it is necessary to keep track of these fluctuations in order to correct for any artefacts that may consequently appear in the experimental data. To aid with this, the FLASH diagnostic system was designed to record as many parameters in the FEL and optical beam lines as possible into one single FLASH data acquisition (DAQ) stream. These beamline parameters were recorded in parallel with the experimental data in a non-intrusive way.

The diagnostic parameters are synchronized to the experimental data by a 32-bit pulse identifier called the BunchID (BID). Therefore, offline analysis can be carried out on the experimental data to account for shot-to-shot fluctuations in the FEL's pulse energy, arrival-time jitter, x - and y -pointing position, photon energy, and its synchronization to the optical laser pulse. The FEL pump-probe data presented in this thesis were corrected for both FEL pulse energy and arrival-time jitter fluctuations

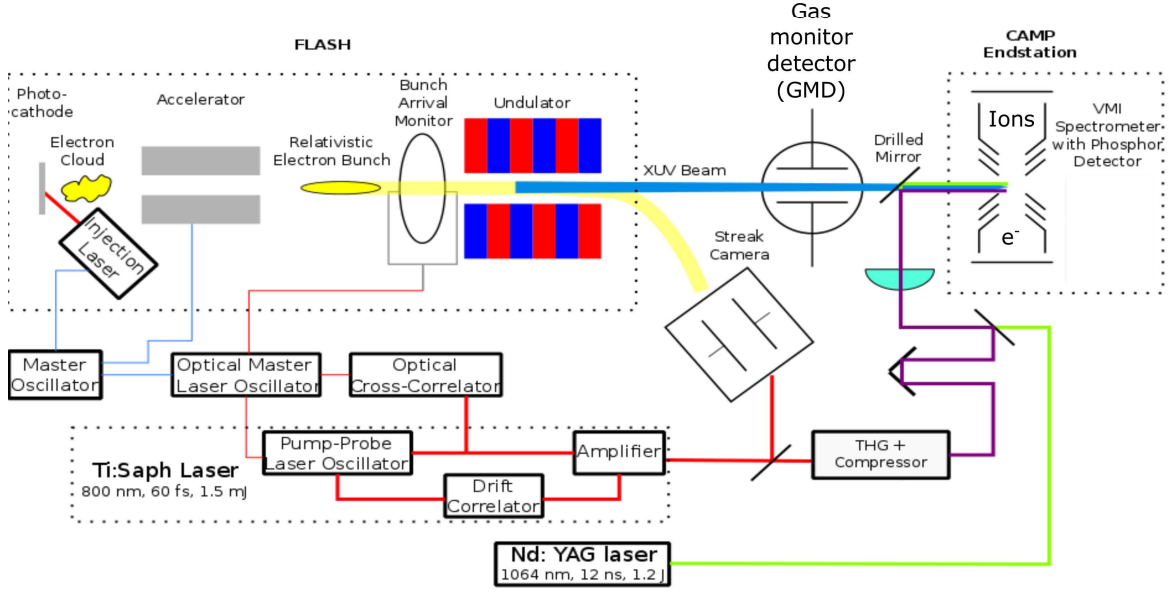


Figure 2.5: A detailed sketch of the optical laser and FEL set-up along with various components of the FLASH diagnostics, timing and synchronization system that played a crucial role in the pump-probe experiments at FLASH. Thick lines are shown for the 1064 nm (green), 800 nm (red) and 267 nm (purple) laser beams. Thin lines are shown for the length-stabilized optical fiber links (red) [169] and the electronic timing connections (blue). This figure was adapted from Reference [84].

as discussed in Chapter 8. Figure 2.5 shows the various components of the FLASH diagnostics, timing and synchronization system, details of which will be given in the following sections.

B1. Gas Monitor Detection (GMD)

The gas monitor detector (GMD) records the FEL pulse energy on a shot-to-shot basis, and was placed between the undulators (long, periodic arrangement of dipole magnets with alternating polarity) and the experimental chamber. The detector was composed of an ionization chamber filled with a noble gas of low enough pressure (typically krypton at a pressure of approximately 2×10^{-6} mbar) such that more than 99% of the FEL pulse passed through the ionization chamber (to reach the experimental chamber) [170]. The less than 1% that was absorbed by the noble gas was enough to generate charged particles. This leads to the build-up of current that was collected by two Faraday cups to give a measure of the FEL's pulse energy [84].

B2. Bunch Arrival-Time Monitor (BAM)

Bunch arrival-time monitors (BAMs) are used to monitor the arrival-time jitter that exists between the FEL and optical pulses. The injection laser, the FLASH accelerator, and the optical master laser oscillator (OMO) are all synchronized to the FLASH master oscillator (FMO) using electronic RF connections, shown in Figure 2.5 (thin blue lines). However, drifts in the arrival-time of both the optical laser and the FEL still appear.

To account for the drifts in the optical laser, an all-optical feedback and stabilization system was used to actively stabilize the optical laser to the OMO with a synchronization time of less than 10 fs (RMS) [171]. In contrast to the optical laser, the FEL generates pulses through spontaneous emission rather than stimulated emission, which makes the FEL an inherently unstable lightsource, as the electron bunches are generated with varying energies. Thus, electrons are accelerated to differing degrees as they travel through the accelerator, generating a variety of arrival-times in the electron bunches. This leads to an arrival-time jitter of approximately 100 fs (RMS) between the electron bunch and the OMO. Although no system was available to actively stabilize the arrival-time jitter of the FEL on a shot-to-shot basis, a correction can be applied during offline analysis [84] to account for this arrival-time jitter [172] (see Chapter 8).

The BAMs record the electrical transient signal from the travelling electron bunch and compare the amplitude of this signal to the synchronized optical laser pulse [84, 172]. The arrival-time jitter between the FEL and optical pulses can be monitored on a shot-to-shot basis with a resolution of down to 5 fs [172]. The BAM resolution for the measurements presented in this thesis was 15 fs, which was limited by the beamline parameters used to obtain FEL pulse with a wavelength of 11.6 nm. The absolute temporal range of the BAMs was limited to 4 ps. To monitor timing fluctuations on a longer timescale, the streak camera was also implemented in addition to the BAMs.

B3. Streak Camera

The streak camera (C5680 by Hamamatsu) is a light-sensitive device that can measure

the intensity of the light pulse as a function of time [168]. It has a working range between 4 ps to 80 ps, and can therefore measure the arrival-time jitter between the FEL and UV pulses on a much longer timescale than in BAMs (up to 4 ps time range) [168]. In order to separate photons from the electron beam in the undulator, the electron bunch is sent around a bent dipole magnet and onto an electron dump. Dipole radiation is emitted by the electrons as they travel around the bending magnet, and is subsequently detected by the streak camera. The output of the optical laser is also detected by the streak camera which allows the relative timing between the FEL and optical pulses to be monitored. The streak camera detects the two radiation sources every two seconds with a temporal resolution of ~ 50 fs (FWHM). Although the streak camera cannot be used in the shot-to-shot timing correction, it does act as a useful diagnostic tool to monitor timing drifts between the FEL and the optical laser over a relatively large dynamic range.

2.4 Velocity-Map Ion-Imaging (VMI) Optics

The trajectory of charged particles was manipulated with electrostatic fields using the method of velocity-map ion-imaging (VMI). In this method, charged particles with the same initial velocity are projected onto the same point on a position-sensitive detector regardless of their starting position in the interaction region, as shown in Figure 2.6.

Single-Sided VMI Spectrometer

A single-sided VMI spectrometer was used in the the Oxford and Aarhus experiments. A schematic of the ion optic assembly used in the Oxford spectrometer is shown in Figure 2.7 consisting of four electrode plates: repeller, extractor, slicing, and grounded electrodes. Each electrode was circular in shape and composed of 1 mm thick stainless steel plates with a central aperture.

The molecular beam was intersected by one or more lasers between the repeller (R) and extractor (E) plates. The voltages applied to the electrostatic plates have the same polarity as the charged particle (*i.e.* positive voltages for positively charged ions and

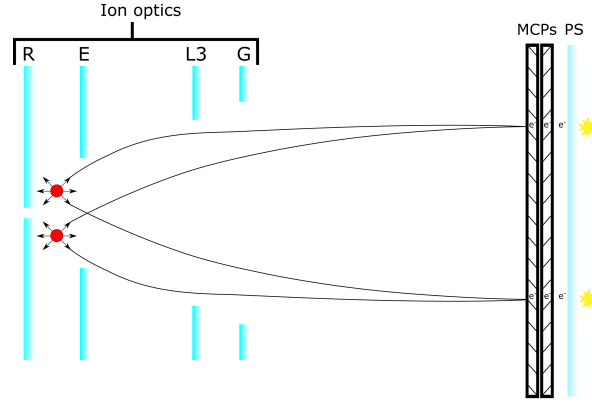


Figure 2.6: The principle of velocity-map ion-imaging (VMI). Charged particles (red circle) are generated between the repeller (R) and extractor (E) plates, with their trajectories (black curved lines) manipulated using electrostatic fields created between the first three electrodes. Particles with the same initial velocity are mapped onto the same point on the detector regardless of their starting position in the interaction region. Once particles impact onto the front of the detector, a flash of light is generated by the scintillator screen. An imaging detector is typically composed of dual-stacked microchannel plates (MCPs) and a phosphor screen (PS). In this particular ion optic design, a third lens plate (L) and a grounded plate (G) are also present.

negative voltages for electrons). The repeller plate repels away any charged particles with the same polarity that approach it. A lower voltage was applied to the extractor plate relative to the repeller plate. This creates an electrostatic potential that extracts charged particles out of the interaction region as they roll down a ‘potential energy hill’ and are subsequently accelerated towards the detector.

A third lens (L) plate is used as an electrostatic focusing lens to minimize the spatial spread of charged particles with the same initial velocity; the third lens plate has a lower voltage than the extractor plate. The grounded plate (G) was kept electrically grounded such that the charged particles traverse through a field-free region as they fly towards the detector. The extractor, lens and grounded ion optic plates have a narrow stainless steel cylinder mounted onto their steel plate with a 3 mm gap between the cylinders as shown in Figure 2.7. The cylindrical plates protect against stray electric fields that can perturb the trajectories of the charged particles.

The ion optics were operated in either velocity-map ion imaging or spatial imaging modes. In the former, either crushed or DC slice imaging VMI modes were employed (see Chapter 3 for further details). In crushed imaging VMI mode, the following voltages in the $V_R : V_E : V_L : V_G$ ratio were applied to the four elec-

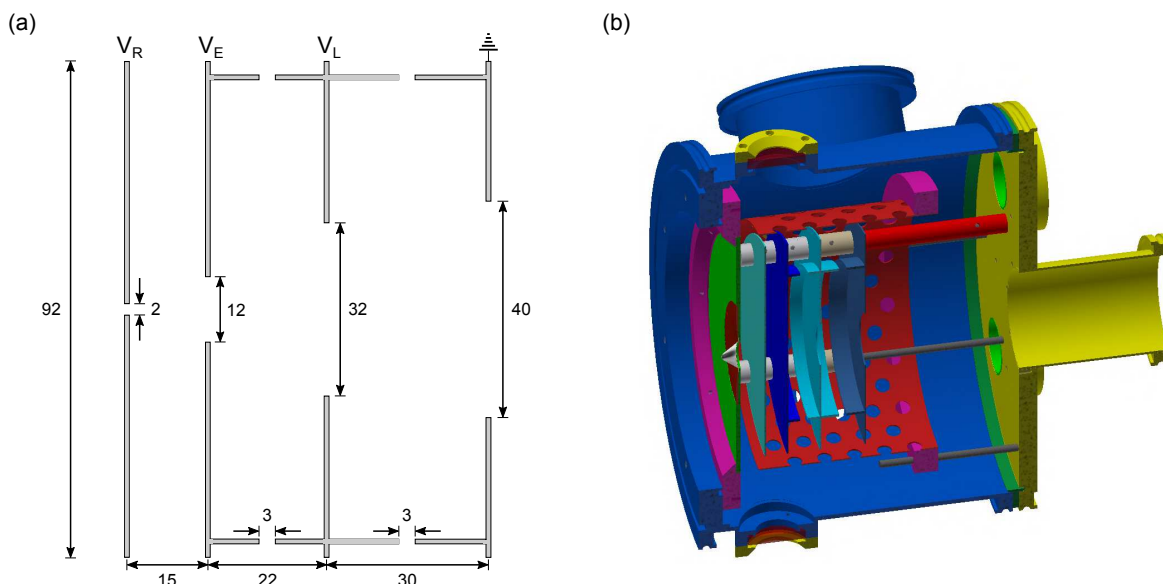


Figure 2.7: The ion optics arrangement used in the Oxford spectrometer is illustrated through (a) a two-dimensional schematic and (b) a side-on three-dimensional model. The four circular-shaped electrodes are: the repeller (R), extractor (E), lens (L) and grounded (G) electrodes. Each electrode contains an aperture in the centre of the electrode, with all measurements given in mm.

trodes: 1.000:0.498:0.000:0.000. Whilst in DC slice imaging VMI mode, the ratio of 1.000:0.886:0.775:0.000 was used. In spatial imaging mode, a ratio of 1.000:0.953:0.000:0.000 was employed. This was typically used to optimize the overlap of lasers with the molecular beam. The optimum potentials were modelled by ion trajectory simulations using SIMION 8.1 [173], and were verified in the laboratory.

In the Aarhus spectrometer, a similar ion optic assembly design was used to that of the Oxford spectrometer but without the third electrostatic lens (L). The Aarhus spectrometer was operated under crushed imaging VMI mode using the following $V_R : V_E : V_G$ ratio of 1.000:0.660:0.000.

Double-Sided VMI Spectrometer

A double-sided VMI spectrometer [146, 174, 175] was employed in the FLASH experiments, as shown in Figure 2.8. In this set-up, the ToF axis was perpendicular to the propagation axis of the molecular beam, and the ions (electrons) were extracted up (down) towards their corresponding detectors. The charged particles were extracted out of the interaction region by accelerating the particles towards an oppositely charged ion optic assembly (*i.e.* positively charged electrostatic plates on the electron side, and

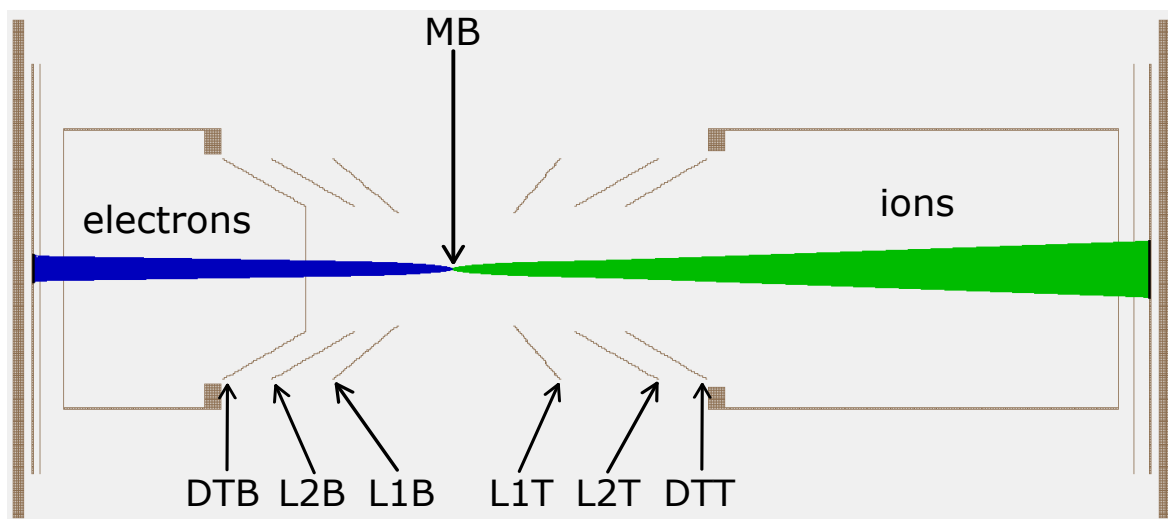


Figure 2.8: Two-dimensional cuts of the VMI double-sided spectrometer in the FLASH experiments. The trajectories of electrons (blue) and positively charged ions (green) are shown along with the direction of the molecular beam (MB) given by the black arrow. The SIMION design of the ion optics was generated by Cédric Bomme.

negatively charged plates on the ion side).

Each assembly consisted of three conical-shaped electrodes, as seen in Figure 2.8. The first and second electrostatic plates on the ion (electron) side are referred to as the L1T (L1B) and L2T (L2B) plates, while the drift tube on the ion (electron) side is referred to as DTT (DTB). The ToF tube for both the electron and ion sides were terminated by a copper grid with approximately 78% transmission in front of the particle detectors. Although the conical-shaped electrodes were originally adapted for diffraction experiments that were coupled with a pnCCD photon detector, no such diffraction experiments were carried out or presented in this thesis.

2.5 Particle Detectors

The position- and time-sensitive detectors used in this thesis consisted of a set of dual-stacked microchannel plates (MCPs) and a phosphor screen. As an ion impinges onto the front MCP, a cloud of secondary electrons is generated within the pores of the MCP. These secondary electrons then impinge onto the second MCP and subsequently generate even more secondary electrons, that lead to the amplification of the ion signal by an order of 10^6 . The secondary electrons impinge onto the phosphor screen to

generate a flash of ultraviolet light, which is detected with either a photomultiplier tube or a camera. Specific details of the particle detectors used in the three spectrometers is given below.

Oxford Particle Detector

In the Oxford VMI spectrometer, a pair of 75 mm chevron-stacked MCPs coupled to a P47 phosphor screen (Photonis USA Inc.) were used. The MCPs have a $25\text{ }\mu\text{m}$ pore size, $32\text{ }\mu\text{m}$ pitch, a bias angle of 8° , and an aspect ratio of 60:1. The pitch size is the centre-to-centre spacing between two pores, with the diameter of a pore given by the pore size. The bias angle is the angle between one MCP relative to the normal of the second MCP, and controls the angular dependency of detection. The aspect ratio is the length-to-diameter ratio of a pore, with a larger ratio leading to greater sensitivity to detection of particles. The front MCP is also coated with gold to ensure faster replenishment of the MCP channels and therefore avoiding saturation of individual MCP pores in a regime of high ion flux.

Aarhus Particle Detector

In the Aarhus spectrometer, dual chevron-stacked MCPs (El-Mul Technologies B050V, chevron MCP with 38 mm active diameter) were used with a P47 phosphor screen (El-Mul Technologies, ScintiMax P47). A voltage difference of around 1800 V was applied across the MCPs, with a voltage difference of 3000 V used between the back face of the back MCP and the phosphor screen.

FLASH Particle Detector

In the FLASH spectrometer, the ion detector was identical to that used in the Oxford spectrometer, while the electron detector consisted of a dual chevron-stacked MCPs (40 mm diameter) coupled to a P20 phosphor screen. A voltage difference of around 1750 V was used across the MCPs, while a voltage difference of around 2400 V was used between the back face of the back MCP and the phosphor screen.

2.6 Spatial and Temporal Overlap

To illustrate the procedure for finding temporal and spatial overlap between the molecular beam and two laser pulses, the pump-probe experiments carried out at FLASH are used as an example. Since the FEL cannot be moved in space or time, precision stepper motors were used to adjust the CAMP end-station chamber in all three spatial dimensions, so that the chamber was aligned with the FEL beam. This alignment was optimized by operating the FLASH spectrometer in spatial imaging mode to image background ions (such as water) that were generated by the FEL pulse, and are typically observed as a line in the detector image. The chamber was adjusted such that the line was centred on the detector image corresponding to the centre (and coldest part) of the collimated molecular beam. The intensity of the spatially-mapped line was optimized by moving the molecular beam relative to the FEL pulse.

Once the chamber and the molecular beam were aligned with the FEL pulse, the Ti:Sa optical pulse was introduced into the chamber. A coarse alignment of the optical pulse was carried out by making sure it traversed through the centre of the entrance and exit chamber windows. The optical pulse was then overlapped with the molecular beam to generate a second spatially-mapped line. The overlap between the molecular beam and the optical pulse was optimized until this second spatially-mapped line (optical pulse) overlapped perfectly with the first spatially-mapped line (FEL pulse).

The temporal overlap between the FEL and Ti:Sa pulses, t_0 , was roughly found by monitoring the arrival-times of both pulses using a fast photodiode with a precision of approximately 20 ps. The temporal overlap was then improved to a much higher precision using the two-colour (UV-XUV) molecular beam signal in velocity-map ion-imaging (VMI) mode. The two-colour signal in the FLASH experiments usually appeared as a low kinetic energy release (KER) channel that corresponded to the photodissociation of a carbon-iodine bond in the molecule [77, 81]. The delay stage was adjusted such that the optical pulse arrived in the interaction region approximately 100 ps before the FEL pulse, which is denoted as UV-early from henceforth. At this UV-early delay, the two-colour low KER channel should appear as a central spot in the detector image. The delay was then adjusted so that the temporal window corre-

sponding to UV-early and UV-late was narrowed to converge onto t_0 with a precision of approximately 100–200 fs.

2.7 The PImMS Camera

The PImMS camera [105, 110, 112, 114, 115, 176, 177] forms the main basis of the work presented in this thesis. It is a time-stamping device that can record the x - and y -position and arrival-time, t , of an event. The PImMS sensor consists of an array of independent pixels (72×72 and 324×324 in PImMS1 and PImMS2, respectively) and is mounted inside of a camera housing with a camera lens attached to it. A LabVIEW interface is used to record data from the PImMS sensor as a 5-element data point (x, y, t, n, m) , where the position and arrival-time of an event is given by x , y , t , the laser shot number is n , and m is the digital register number (1 – 4) in which the arrival-time was stored in. A large volume of data is typically generated by this sensor, and requires very high data transfer rates and the ability to store information (such as the arrival-time) locally within each pixel. Achieving this requires complicated electronics to be incorporated within each pixel, details of which have been previously discussed in Reference [178], and are outside of the scope of this thesis.

A brief description is given on the operating principle of a PImMS1 pixel, with an overview shown in Figure 2.9 [177]. When photons impact onto a pixel, charge begins to build-up in the four collection diodes that generate a weak voltage pulse, V_D . A pre-amplifier intensifies this weak pulse from the sum of all four diodes into a larger voltage pulse, V_{PA} , that is inverted. A CR-RC shaper then generates two voltage pulses, V_{S1} and V_{S2} , which are further amplified. As each pixel operates independently, they each have a different sensitivity to the detection of a photon. A comparator trim block is used to ensure that each pixel has the same sensitivity by thresholding and trimming the two voltage pulses to give V_{C1} and V_{C2} . These two pulses are then compared to each other using a comparator to determine whether the event that generated the voltage pulse V_D in the pixel is above an externally set threshold. If it is, then a voltage pulse, V_O , is sent to the digital controller and the value of the global 12-bit timer is locally

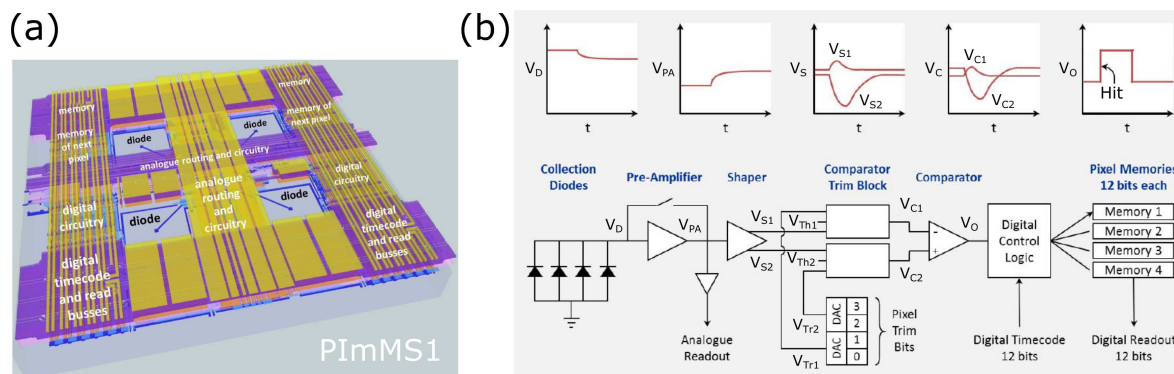


Figure 2.9: (a) A schematic of a PImMS pixel is shown which comprises of four photodiodes and digital memory registers where up to four timestamps are locally stored on the pixel. (b) The operating principle of a PImMS1 pixel is shown.

stored as a digital time-stamp in one of the four digital memory registers with 12.5 ns timing precision in the affected pixel. The remaining three digital memory registers in the pixel are then subsequently filled when further events are detected above the externally-set threshold in the same experimental period.

2.7.1 Cluster Analysis

A single ion impact onto a detector can lead to the illumination of multiple pixels within the camera, which is referred to as a cluster of pixels. The size of the cluster is dependent on both the force and location of impact on the front MCP (*i.e.* whether it impacted directly inside the pore or between pores). Some control over the size of the cluster does exist by varying the potentials applied to the detector [179, 180], with higher potentials generally yielding a larger pixel cluster for each ion signal. A range of cluster sizes were recorded within one PImMS dataset as shown in the histogram plot of cluster sizes in Figure 2.10(a). There is a significant contribution from single pixel clusters to the total distribution as single pixels may be triggered randomly and independently from the ion signal. These are referred to as noisy pixels. Ignoring these noisy pixels, the histogram can be described by a Poisson distribution. Poissonian statistics are typically observed in ion imaging experiments with dilute gaseous samples (*i.e.* low probability of fragmenting the target molecules) since the variance of the number of molecules fragmented is equal to its mean [124].

By analysing these clusters of pixels, a single accurate arrival position may be

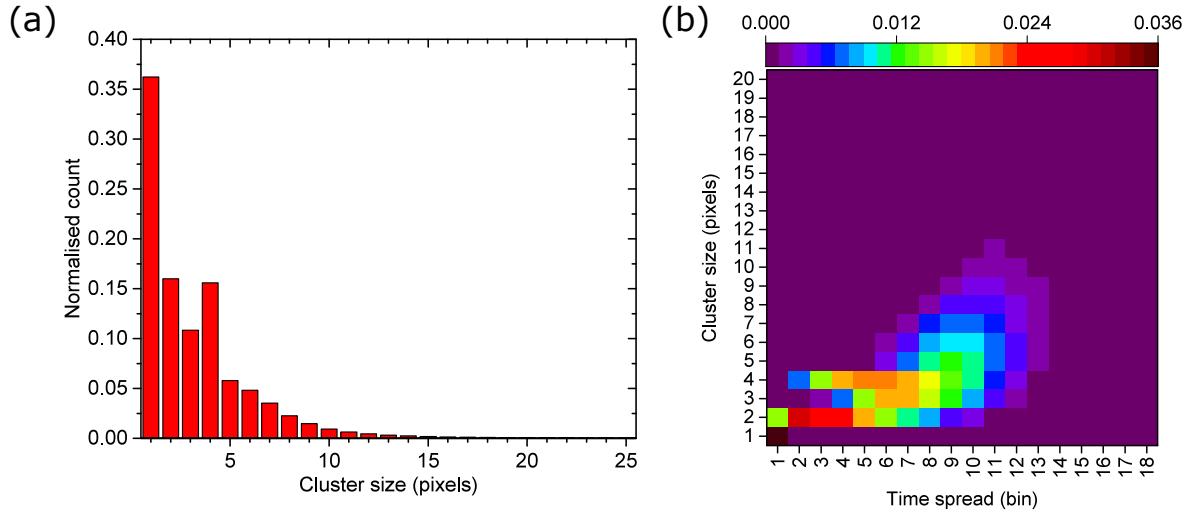


Figure 2.10: (a) Histogram of the number of times a cluster of pixels appears in a PImMS1 dataset. (b) A two-dimensional heatmap plot of cluster size against time window corresponding to the one-colour photolysis of OCS at 230 nm recorded with the PImMS1 camera.

determined through various centroiding or ‘ion counting’ algorithms [107, 181, 182]. In the case of a time-stamping device, such as the PImMS camera, both the position and arrival-time of ions are recorded. This leads to the added complexity that a single ion generates a cluster of pixels with a variety of arrival-times. This is due to the brighter (dimmer) parts of the flash of light going over threshold quicker (slower) thus leading to the recording of an earlier (later) timecode. The difference between the minimum and maximum timecode within a cluster is referred to as the time spread. Figure 2.10(b) shows a plot of the time spread within the cluster against a range of cluster sizes. An increase in cluster size is accompanied by a larger time spread within the cluster.

Centroiding

The method of centroiding reduces a cluster of pixels to a single pixel with an accurate position and arrival-time. Unless otherwise stated, the data presented in this thesis was centroided using an algorithm developed previously [54, 56, 183]. A brief description of the algorithm is given below.

1. The earliest time code in the cluster, t_0 , was taken as the true arrival-time of the ion.

2. Each pixel within the cluster was assigned a weighting, w_i , defined as:

$$w_i = \frac{1}{t_i - t_0 + 1}, \quad (2.3)$$

where t_i is the time code recorded in pixel i .

3. A single accurate coordinate was calculated based on the weighted average of each pixel within the cluster given by:

$$c = \frac{\sum_{i=1}^N r_i w_i}{\sum_{i=1}^N w_i}, \quad (2.4)$$

where r_i is the coordinate of pixel i , and N is the total number of pixels within the cluster. Figure 2.11 illustrates the effect of centroiding on the ToF profile for CO^+ ions formed in the one-colour photolysis of OCS at 230 nm, with several improvements observed [183]. A narrower and more symmetric ToF profile is generated which was

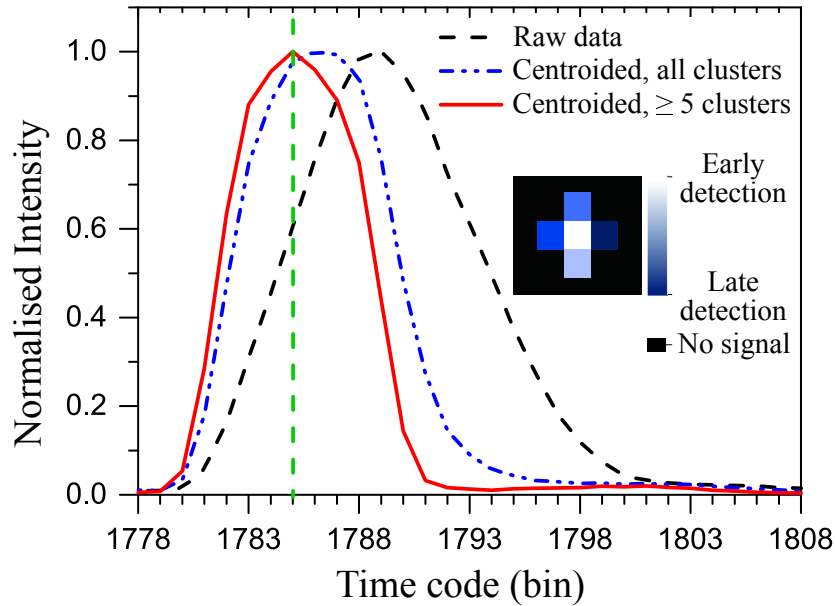


Figure 2.11: The ToF profiles for CO^+ ions following the photolysis of OCS at 230 nm recorded with the PImMS1 camera. The profile corresponds to the raw data (black dashed trace), centroided data (blue dashed-dot line), and centroided data with a minimum of five pixel clusters (red solid trace). The centre of the latter data is indicated by the green vertical dashed line. A typical cluster of five pixels is shown in the inset, with the various arrival-times of the pixels in the cluster given by the colour coding.

shifted to earlier time codes after centroiding all pixel clusters (blue line in Figure 2.11). A small tail still exists in the late part of the ToF profile due to the dimmer signals from the phosphor screen.

Pixels in small clusters take relatively longer to go over threshold, which leads to a greater uncertainty in the ion arrival-time. If only clusters containing five pixels and above are analysed, a nearly symmetric ToF profile is achieved (red line in Figure 2.11). This clearly shows that brighter signals from the phosphor screen, which impact more PImMS pixels, go over threshold quicker, with a time-stamp recorded very close to the actual arrival-time of the ion at the detector, t_0 . Unless otherwise stated, images from the centroided data were symmetrized since the system was cylindrically symmetric around the ToF axis, improving the signal-to-noise in the data. Images were symmetrized by calculating the average of the four quadrants in the ion image, with the averaged data replacing the raw data in each of the four quadrants.

Mega-pixel Imaging

Once a more accurate position is calculated using Equation 2.4, the new position was mapped onto a finer grid of points with a higher resolution than a single pixel from the original sensor. This is called mega-pixel imaging [182, 184]. Figure 2.12 shows the ion images from raw, centroided and mega-pixel data following the one-colour photodissociation and ionization of OCS at 230 nm recorded with the PImMS1 camera. Here, the features in the CO^+ ion image are well-resolved after centroiding of the raw data, as shown in the second column. The third column shows the result of centroiding the data into a ‘virtual’ pixel array with twice the dimensions of the sensor (*i.e.* 144×144 pixels), generating better-resolved ion image when compared to the standard centroided case. Although a ‘virtual’ pixel array of even higher dimensions can be generated, artefacts begin to appear in the form of gridded patterns in the mega-pixel image, as shown in the fourth column. Thus, a mexapixel factor of two was used in the centroided data presented in this thesis.

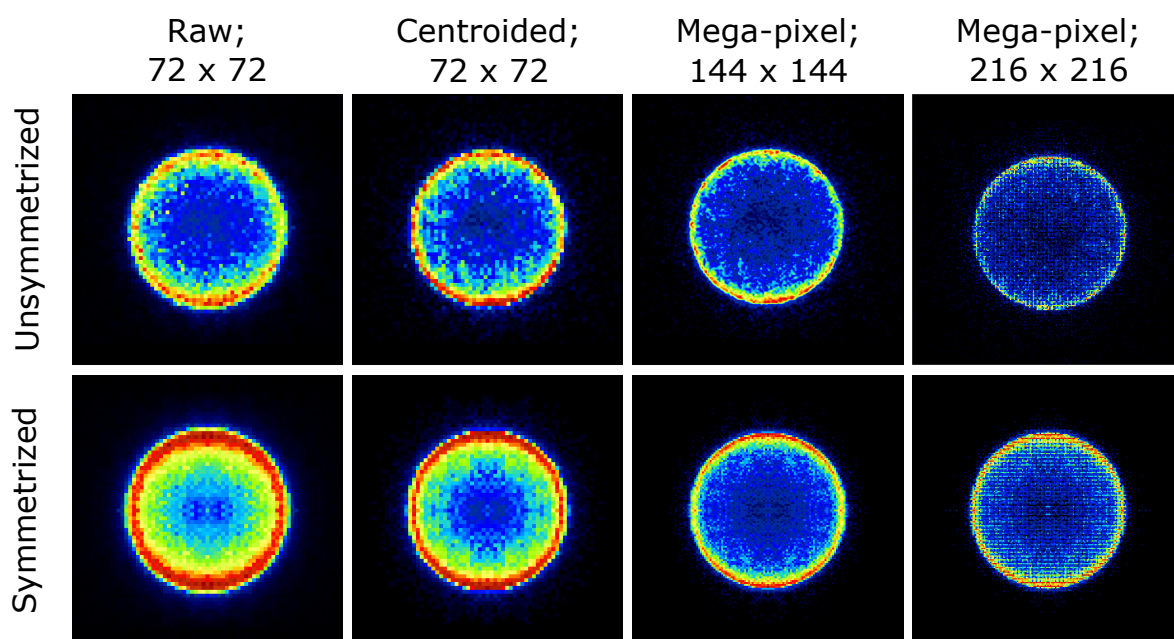


Figure 2.12: A collection of CO^+ ion images from the one-colour photodissociation and ionization of OCS at 230 nm recorded with the PImMS1 camera. The top and bottom rows show the unsymmetrized and symmetrized ion images, respectively. Each column from left to right shows: raw, centroided, and mega-pixel data using megafactors 2 and 3.

2.8 Reagent Sources

In the 3D imaging measurements in Chapter 3, gaseous carbonyl sulphide (OCS) was studied. To limit the formation of clusters, the gas mixture concentration was kept sufficiently low ($< 10\%$ OCS seeded in He at a backing pressure of 1.5 bar). In all other measurements, the samples used are liquids at room temperature. The samples were applied to a filter paper and placed inside the inlet compartment of an Even-Lavie valve. The valve was heated to 70–150°C in order to generate a gaseous sample in a high-pressure of inert carrier gas (20–80 bar). The *trans*-4,4'-difluoroazobenzene molecule was synthesised specifically for the experiment. The isomers of difluoriodobenzene and dihydroxybromobenzene were commercially available and were purchased from Sigma Aldrich.

In the static isomer measurements in Chapter 5, switching of molecules occurred frequently, and it was crucial that the sample reservoir was clean and background-free before changing to a new molecule. The internal reservoir of the valve was cleaned with acetone, sonicated for 30 minutes, and the empty sample reservoir was heated for

1 hour at 100 °C. The new sample was then loaded and new measurements were carried out.

2.9 Summary

In summary, a detailed discussion of the experimental principles and apparatus used in this thesis was given in this chapter. In the following chapter, the 3D imaging capability of the PImMS camera is demonstrated in the one-colour photodissociation of OCS using the Oxford VMI spectrometer.

Chapter 3

Three-Dimensional Velocity-Map

Imaging of OCS

The work presented in this chapter demonstrates the three-dimensional (3D) imaging capability of the PImMS camera by recording the full 3D velocity distribution of fragment ions following the one-colour photodissociation of carbonyl sulphide (OCS) at 230 nm. In addition to the x - and y -direction, the PImMS [109–111, 113, 115, 116] camera can detect the time-of-arrival of a particle with a precision of down to 12.5 ns. Consequently, data acquisition with the PImMS camera is not restricted to a specific ToF window, as is the case with CCD cameras which are time-gated. Thus, the PImMS camera can record all ions simultaneously under the same experimental conditions. Using a time-stamping device such as the PImMS camera also bypasses the restriction of cylindrical symmetry, which is typically required to reconstruct 3D velocity distributions from two-dimensional (2D) projections.

Two generations of the PImMS camera (PImMS1: 72×72 pixels; PImMS2: 324×324 pixels) were used in the proof-of-principle 3D imaging experiments, with the OCS molecule, whose photodissociation dynamics have been discussed in detail previously by a number of authors, chosen as our exemplary system [20, 185–208].

3.1 Introduction to Ion Imaging

In the photodissociation of molecules, fragments are generated with a 3D velocity distribution based on their initial kinetic energy and angular distribution. If the fragments contain a distinct kinetic energy release then a spherical distribution of ions is formed in three-dimensional space, called a Newton sphere. To preserve the initial 3D velocity distribution from the photodissociation process, the fragments are ionized and their trajectories are manipulated using electrostatic fields to project the charged fragments towards a position-sensitive detector [13, 14].

Chandler and Houston [14] demonstrated the first experiment to capture the velocity distribution of photofragments after the photodissociation of the target molecule by using electrostatic fields to manipulate the trajectory of the subsequent charged fragments generated by the probe pulse, which led to the field of ion imaging. Charged fragments were generated between a charged grid, called the repeller grid, and a pair of grounded grids such that the charged fragments were accelerated towards an imaging detector [14]. The recorded velocity distribution was significantly blurred because of two reasons. Firstly, only a single charged electrode was used which was not enough to compensate for the varying starting positions of fragments with the same initial velocity in the interaction region [14]. Secondly, the gridded electrodes perturbed the trajectory of the charged particles as they passed through the gridded wires [13]. Eppink and Parker later demonstrated a significant improvement in the quality of the 2D detector image through the method of velocity-mapped ion imaging [13].

3.1.1 Velocity-Map Ion-Imaging (VMI)

In velocity-map [13] ion-imaging [14] (VMI), particles that have the same initial velocity are detected at the same position (and at the same time) on the detector regardless of their initial starting position in the interaction region [13]. Eppink and Parker not only used open electrodes instead of their gridded counterparts, but they also used two charged electrodes instead of one. The addition of a second electrode enabled the extraction of charged particles from the interaction region with a velocity that was

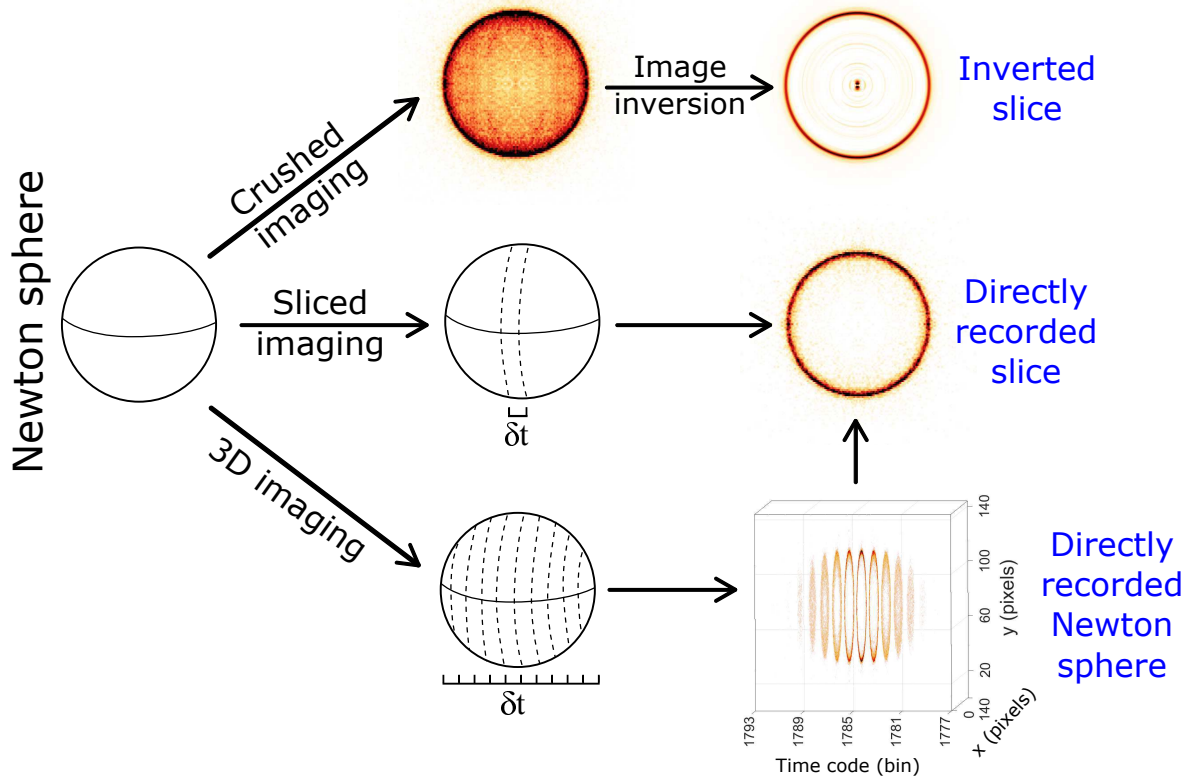


Figure 3.1: The three types of VMI imaging: crush, slice and 3D imaging.

dependent on the photodissociation process, with no contribution from the electrostatic fields. The two charged open electrodes are used as electrostatic lenses by simply varying the voltages that are applied to them, which provides control on how well particles with the same velocity are focussed onto the same position on the detector. As shown in Figure 3.1, several variations of VMI exist, namely: crushed, sliced and 3D VMI imaging. Details of these are given in the following sections.

3.1.2 Crushed VMI

In crushed VMI, the three-dimensional velocity distribution is projected onto a two-dimensional detector to produce a 2D “crush” ion image. If the system is cylindrically symmetric, the full three-dimensional velocity distribution can be reconstructed from the 2D crushed ion image using various reconstruction methods [209–213], based on the inverse Abel transform [214, 215]. An infinitely thin slice along the ToF coordinate, δt , is extracted from the central portion of the reconstructed velocity distribution. This generates an inverted slice image, due to cylindrical symmetry, which contains all

the kinetic energy and angular information that is present in the full distribution. A major drawback to using these reconstruction methods is the introduction of noise and artefacts into the reconstructed images, which typically appear as an intense central spot or along the centerline, which makes these regions of the image unusable.

3.1.3 Sliced VMI

In sliced VMI, a finite slice along the ToF coordinate from the full 3D velocity distribution is directly recorded to bypass the need for cylindrical symmetry and the use of reconstruction algorithms. Although several variations of sliced VMI imaging exist [142, 199, 216–218], they all follow the same fundamental principle of gating the detector for a short period of time (the so-called gate width, δt), thus allowing to record only the central slice of the Newton sphere. The most commonly used approach is “DC sliced imaging”, which was developed independently by Townsend *et al.* [142] and Lin *et al.* [217]. In both approaches, the ion cloud was stretched in all dimensions to generate a Newton sphere with a total ToF spread (Δt) of ~ 250 ns. The detector was gated with a width δt of 40 ns to record a thin slice through the centre of the Newton sphere, with an overall slicing resolution $\delta t/\Delta t$ of 0.16. A better slicing resolution of 0.075 was achieved by Lipciuc and coworkers [199] by using a gate width of 12 ns along a Newton sphere that spanned ~ 160 ns.

In the approaches discussed so far, a microchannel plate (MCP) and phosphor screen detector was used to detect charged particles which, upon impingement of the electron cloud on the phosphor screen, emit flashes of light that are typically recorded by a charged-coupled device (CCD) camera. Due to the limited frame rate of this type of camera, only one crushed or sliced image can be recorded per acquisition cycle for a given ToF window. Rather than recording a crushed or sliced image, it is desirable to record the full 3D recoil distribution of particles. This is especially true in the situation in which the Newton sphere of ions does not possess cylindrical symmetry, for example, as a result of inelastic scattering of two particles [219, 220] or photofragment angular momentum alignment or orientation [163, 212, 221, 222]. It is possible to use a sliced imaging set-up to record a series of slices through the 3D distribution by

stepping the detector gate across the arrival-time distribution of ions. However, this is a slow process and may lead to significant distortion of the measured 3D distribution due to experimental drifts that may occur over time. A more efficient approach is the simultaneous recording of the time and the position of the ions arriving at the detector.

3.1.4 3D VMI

In 3D imaging, the full 3D distribution of ions is directly recorded in a single measurement. To achieve this, a detector that is both position- and time-sensitive is required to record the particle's x - and y -position as well as its arrival-time, t . Several types of detectors have been developed and employed for 3D imaging and are usually based on either a delay-line anode (DLA) or event-triggered pixel-based sensors [89, 91–99, 101–104, 108, 110, 115, 223]. Delay-line anodes [89, 91–99] have been employed in 3D velocity-map imaging experiments [224–226] carried out under low count-rate conditions. Multiple mass-to-charge (m/q) fragments can be recorded with a hexanode delay line detector [96, 99]. However, the hexanode detector has been shown to record only up to tens of ions from the same m/q fragment in each acquisition cycle [96, 99]. Event-triggered ‘intelligent’ pixel detectors, such as the PImMS or TimePix sensors, solve this multi-hit problem by integrating timing measurements into each pixel. Thus, the arrival-time and position of multiple mass-to-charge fragments can be recorded at relatively high count-rate conditions (>100 ions/shot). A detailed description of these detectors was given in Chapter 1.

Suitable VMI conditions are required to generate a Newton sphere of ions with the largest ToF spread possible to achieve good slicing resolution (*i.e.* $\delta t/\Delta t < 0.10$) in order to maximize the number of slices that can be recorded through the Newton sphere by the position- and time-sensitive detector.

In this chapter, the PImMS1 (72×72 pixels) and PImMS2 (324×324 pixels) time-stamping cameras are implemented with a DC sliced imaging VMI set-up to capture the full 3D velocity distribution of a photodissociation process by recording multiple slices through the Newton sphere of ions.

3.2 Experimental Methods

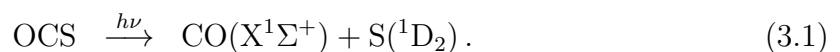
A brief overview of the experimental parameters used are given in this section, with further details found in Chapter 2. A sample gas mixture containing 10% OCS seeded in He to a total pressure of 1.5 bar was expanded through the nozzle of a pulsed General Valve (Series 9) valve. The resulting molecular beam was intersected by a 230 nm pulse with a typical pulse energy of $60 \mu\text{J}$. The polarization of the pulse was switched on alternate shots to lie either parallel or perpendicular to the plane of the detector using a photoelastic modulator.

The resulting charged particles were velocity-mapped onto a position- and time-sensitive detector using DC slice imaging VMI mode. In this mode, the $V_R : V_E : V_L : V_G$ ratio of 1.000 : 0.886 : 0.775 : 0.000 was used, with an absolute voltage of 1.5 kV applied onto the repeller electrostatic plate.

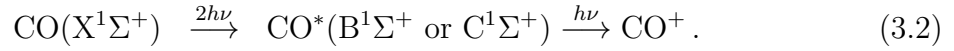
The detector was operated with a potential difference of between 1.80 kV – 1.96 kV applied across the MCPs, while a potential difference of around 3.2 kV was used between the back face of the back MCP and the phosphor screen. The detector was pulsed by pulsing ‘on’ the front MCP plate from 400 V to 0 V in the time-of-flight range of interest, making the detector sensitive to only the ions of interest and nullifying the appearance of background signal such as stray laser light. Flashes of light emitted from the back of the P47 phosphor screen were recorded with either a conventional CCD camera, the PImMS1 camera or the PImMS2 camera.

3.3 Experimental Results

In this section, results from a proof-of-principle 3D imaging experiment are presented for the one-colour photodissociation and ionization of OCS at around 230 nm recorded with the PImMS camera. The parent molecule was photodissociated using a single photon of a wavelength around 230 nm to produce $\text{CO}(\text{X}^1\Sigma^+)$ and $\text{S}(^1\text{D}_2)$ photofragments,



Further photons from the same laser pulse were used to probe the CO products in a specific rotational quantum state (J) *via* (2+1) REMPI [187, 192]



The sulphur photofragments can also be ionized *via* a (2+1) REMPI scheme, using photons of slightly higher wavelengths [114, 187, 192]:



3.3.1 Photofragment Rotational Distribution

Tuning the laser between the wavelength range of 229.8 nm and 230.15 nm generates the REMPI spectra for the CO and S($^1\text{D}_2$) products of OCS dissociation as shown in Figure 3.2(a). The CO($\text{X}^1\Sigma^+; J$) photofragment is generated with a bimodal rotational distribution since OCS can dissociate *via* two distinct dissociation pathways [114, 186, 187, 189, 190, 193, 195, 199, 200, 227, 228]. The ground state of OCS has a linear geometry but upon excitation of the molecule at 230 nm, the $1^1\text{A}''$ and $2^1\text{A}'$ excited electronic states are populated, in which the minimum energy structure has a bent geometry, as shown in Figure 3.2(b).

As the bending molecule separates, a strong torque is imparted onto the fragments to generate CO fragments that are highly rotationally excited but primarily in their ground vibrational state [186, 189, 193]. Thus, dissociation of OCS from both $1^1\text{A}''$ and the $2^1\text{A}'$ surfaces lead to strong rotational excitation of CO products. Figure 3.2(b) also shows that a non-adiabatic transition occurs (red circle) from the $2^1\text{A}'$ excited state to the $1^1\text{A}'$ ground state [189, 195]. As a result, the bending energy gained on the $2^1\text{A}'$ excited state is efficiently transformed into product rotation to generate CO fragments in higher rotational quantum states and subsequently slower S fragments [189, 190, 195, 199, 227, 228].

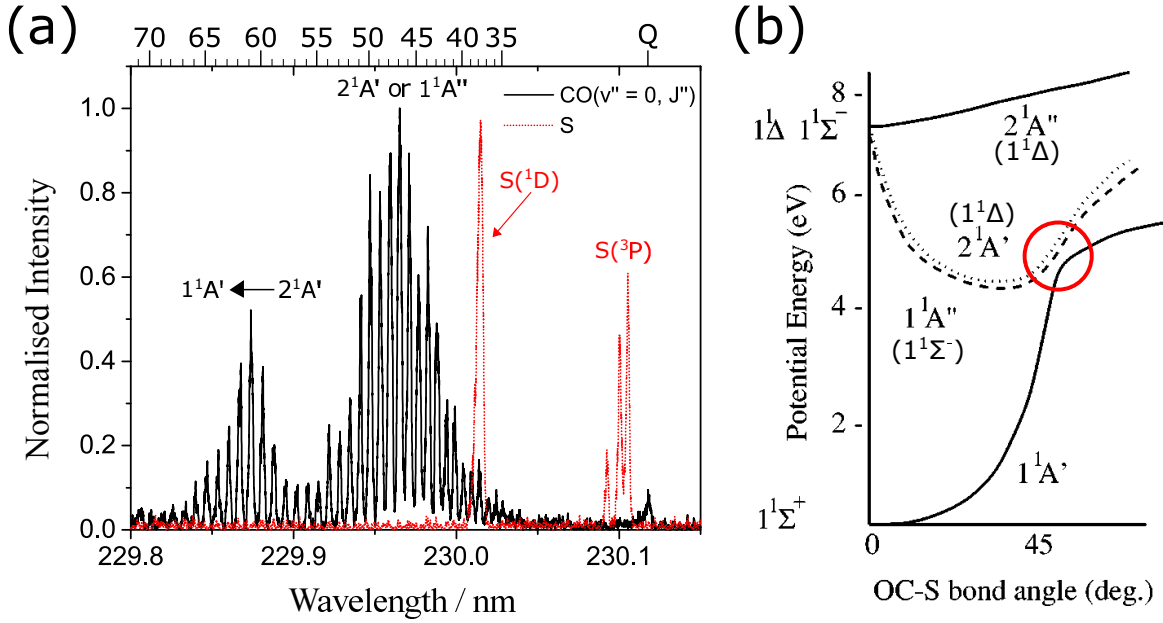


Figure 3.2: (a) REMPI spectra of the CO (black solid line) and S(1D_2) (red dashed line) photofragments following one colour photodissociation of OCS and (2+1) REMPI of the CO and S(1D_2) photofragments in the wavelength range 229.80 nm to 230.15 nm. The rotational quantum states of CO are indicated by the labels at the top of the plot. (b) The potential energy surface of carbonyl sulphide (OCS) as a function of carbon-sulphur bond angle at an equilibrium bond distance is shown here. The red circle indicates a non-adiabatic transition from the $1^1A''$ and $2^1A'$ surfaces to the $1^1A'$ ground state for an excited OCS molecule with a bent (45°) geometry. This figure is adapted from Reference [195].

3.3.2 Quantitative Measures of Performance

To quantify the performance of the PImMS cameras, three measures are used: the velocity resolution, the beta parameter, and the slicing resolution. To characterize how well the PImMS camera captures information of the photodissociation process in the radial (and thus velocity) component, the mean velocity, v , and the full-width half-maximum of the velocity resolution, Δv , are extracted to determine the velocity resolution, $\Delta v/v$, of the measurements [142].

To characterize how well PImMS can extract angular information from the photodissociation process, the spatial anisotropy parameter, β , is extracted, with a comparison also made to literature β values. The angular distribution of photofragments following the photodissociation of a molecule can be calculated using [229]

$$I(\theta, \phi) = \frac{1}{4\pi} [1 + \beta P_2(\cos \theta)] \quad (3.4)$$

where θ and ϕ are the polar angles between the transition dipole moment vector of the photolysis light, ϵ_d , and the recoil velocity of the fragments, $\mathbf{v}$, whilst P_2 is the second Legendre polynomial given by $(1/2)(3x^2 - 1)$. The spatial anisotropy parameter, β , given by

$$\beta = 2 \langle P_2(\cos \theta) \rangle , \quad (3.5)$$

gives an insight into the transition type, and the geometry of the parent molecule immediately prior to dissociation, by considering the angle θ . The β parameter has limiting values of +2 (parallel transitions) and -1 (perpendicular transitions) which correspond to $\cos^2\theta$ and $\sin^2\theta$ distributions, respectively, while a value of 0 corresponds to an isotropic distribution with a mixture of parallel and perpendicular transitions [229, 230].

The slicing resolution, $\delta t / \Delta t$, gives a measure of the slicing performance of the PImMS camera with knowledge of the total ToF spread, Δt , and the timing precision of each time-resolved slice, δt , which in the case of the PImMS cameras is as low as 12.5 ns. A quantitative comparison between the PImMS and CCD cameras is also shown by the inverse Abel transform of their respective crushed ion images. Where necessary, the pBasex algorithm [213] was used to perform the inverse Abel transform, yielding the equivalent of an infinitely thin central slice.

3.3.3 The CO Photofragment

The CO fragment was recorded with the PImMS1 camera in either the $J = 46$ or $J = 59$ rotational quantum state. The former generates an isotropic distribution ($\beta \sim 0.3$) of CO fragments with a very narrow velocity distribution, and can be used to determine the lowest velocity resolution possible. The CO fragments in the $J = 59$ state are generated with a highly anisotropic ($\beta \sim 1.5$) angular distribution, which, as a result, contains a node within their recoil distribution. The node can be recorded in one or more time-resolved slices with the PImMS1 camera by using a photolysis laser with its transition dipole moment vector parallel to the ToF axis. How well-resolved this nodal feature is experimentally can be characterized by comparison to

simulated data that is convoluted in the ToF coordinate, which is investigated later in this chapter. The angular distribution of the two fragments is also extracted from the data and compared to literature values to investigate how accurately the β parameter for isotropic and anisotropic distributions can be measured.

Comparison of Crushed and Sliced Images

Figure 3.3 presents data for the CO($J = 46$) fragment recorded with the PImMS1 camera. Here, the polarization vector of the photolysis light lies in the plane of the detector (‘parallel polarization’), along the vertical axis of the images. The centroided ToF profile shown in panel (a) has a high degree of symmetry as indicated by the broken black line, that is reflected around the peak of the ToF profile. The individual 3D slice images are presented in panel (b), and correspond to the individual time codes indicated by the yellow shading on the ToF profile. The central slice is highlighted by the red bold border at time code 1785. The top row of images in panel (a) show the crushed ion images which have been generated by summing the complete set of individual sliced images.

The centroided crushed image is significantly better resolved than the raw crushed image, and is comparable to the simulated crushed image, details of which are given in Section 3.4.2. The centroided central slice before and after symmetrisation is shown in the second row of images in panel (a), along with the reconstructed central slice from the pBasex-inversion of the centroided crushed image. Symmetrisation leads to improved signal-to-noise. The directly recorded and reconstructed sliced images have a very good agreement with one another, although noise and other artefacts appear in the latter due to the Abel inversion process. The speed distributions from these two sliced images are presented in Figure 3.4(a) and are accompanied by the distribution of the simulated slice. All three distributions have a speed resolution of ~ 0.06 , which confirms that the PImMS1 camera can directly record a radial distribution that is as well-resolved as the reconstructed distribution using the pBasex algorithm.

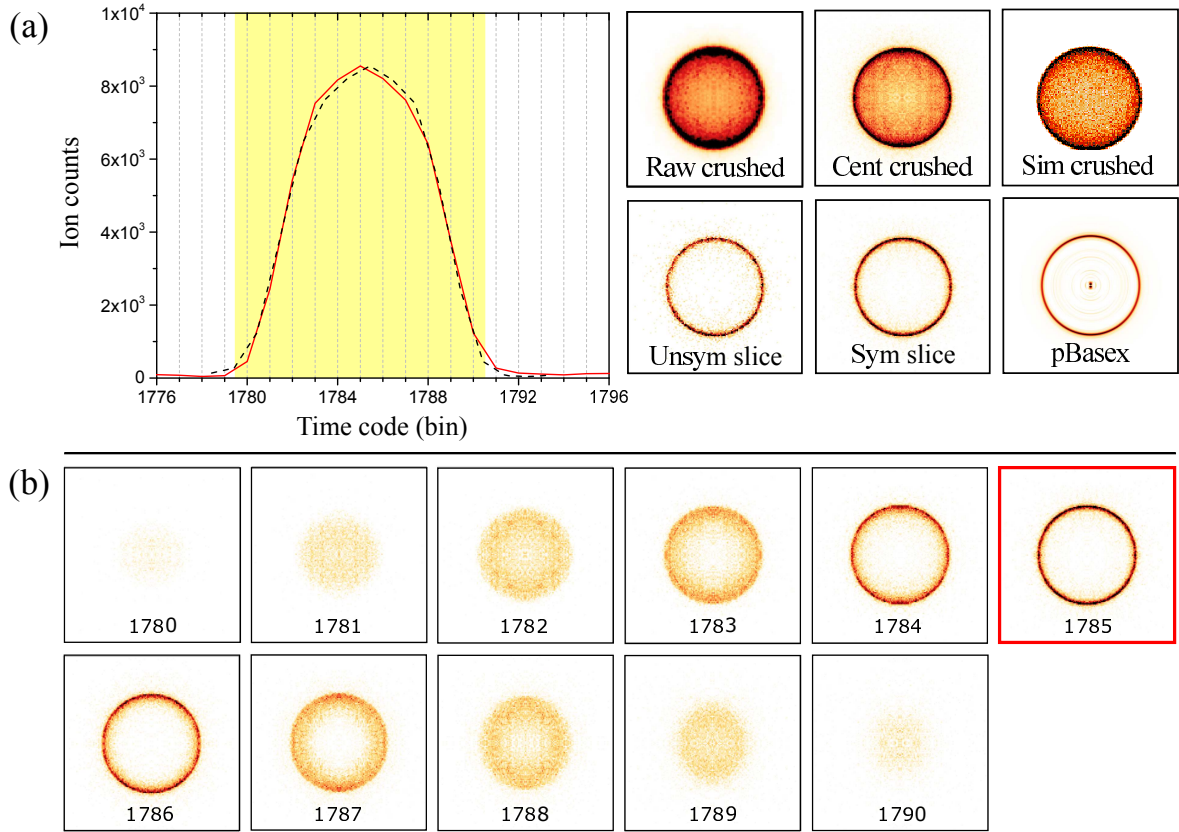


Figure 3.3: Ion images of CO photofragments produced following the photodissociation of OCS at 229.95 nm, probing the $J = 46$ quantum state, as recorded with the PImMS1 camera. Panel (a): The left panel shows the ToF peak of CO^+ ions (solid red line). The ToF profile is also shown reflected around the line center (broken black trace) to give an indication of the degree of symmetry in the data. The range of time bins plotted is indicated in the ToF profile by the yellow shading. Small time-codes represent early events, and each time bin spans 12.5 ns. The six ion images at the top right of the figure correspond to the raw crushed, the centroided crushed, and the simulated crushed images (top row), and the pre- and post-symmetrized centroided central slice, and the pBasex-inverted image (bottom row). Panel (b): The individual time slices, with each number indicating the time bin of the slice image. The central slice is indicated by a bold red border at time code 1785. Only clusters of more than four pixels were included during centroiding.

3D Slice Images

A closer look at the individual sliced images in Figure 3.3(b) reveals that 11 time-resolved slices were recorded through the Newton sphere of ions, corresponding to a total ToF spread, Δt , of 137.5 ns. Since each time-slice, δt , spans 12.5 ns, a slicing resolution, $\delta t/\Delta t$, of approximately 9% was achieved. Therefore, each 12.5 ns sliced image recorded by the PImMS1 camera captures ion events corresponding to $\sim 9\%$ of the full width of the ToF peak. By stacking all the individual sliced images from

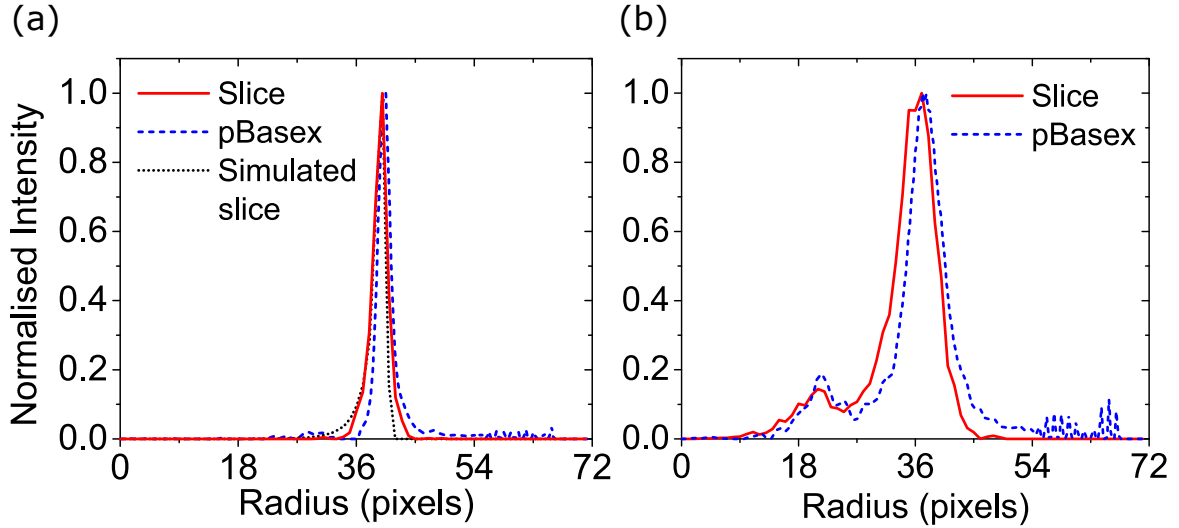


Figure 3.4: The speed distribution extracted directly from the PImMS1 central slice (red continuous line), and the speed distribution obtained from the pBasex inversion of the PImMS crushed ion image (blue dashed-dotted line) for (a) the $\text{CO}(J = 46)$ and (b) the $\text{S}(^1\text{D}_2)$ photofragments following the one colour molecular photodissociation of OCS at 229.98 nm and 230.01 nm, respectively. In panel (a) the black dotted trace shows a simulation of the expected speed distribution obtained from the PImMS central slice. Errors in the pBasex data are typically around 5% at the peak of the distribution.

Figure 3.3(b), a four-dimensional (4D) plot, $I(x, y, t)$, of the Newton sphere of ions can be generated as shown in Figure 3.5(a) for $\text{CO}(J = 46)$ and in panel (c) for $\text{S}(^1\text{D}_2)$. Panel (b) shows the corresponding simulation results for $\text{CO}(J = 46)$ with a 25 ns convolution applied to the simulated data, details of which are given in Section 3.4. Both experiments and simulations can clearly reproduce the full 3D Newton sphere of

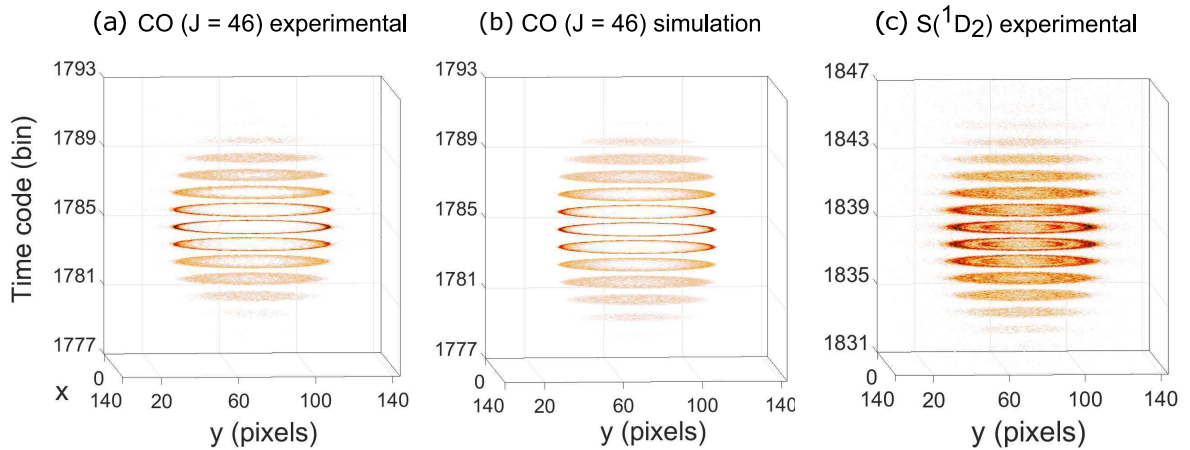


Figure 3.5: 4D plots of (a) the experimental and (b) simulated Newton spheres for the $\text{CO}(J = 46)$ photofragment, and (c) the experimental Newton sphere for the $\text{S}(^1\text{D}_2)$ photofragment. The data were obtained subsequent to the one colour molecular photodissociation of OCS at 229.98 nm and 230.01 nm, respectively.

ions, while the excellent agreement between both results indicates that the performance of the instrument is very well understood.

The β Parameter

To gauge how well the PImMS1 camera captures the angular distribution of the CO($J = 46$) photofragment, the β value is extracted directly from both the central slice at time code 1785 and from the reconstructed slice images. A β value of 0.311 ± 0.005 was extracted from the former, while the latter returned a value of 0.259 ± 0.021 . A small difference between the two values exists, most likely due to the inversion algorithm using the entire data set (the crushed image integrated over the full ToF range of the fragment), whilst the direct approach uses only the central slice. Both values agree well with the value of 0.370 ± 0.050 obtained by van den Brom *et al.* [195], although a perfect agreement between the two experiments would not be expected as the parent molecule in this work was cooled in a molecular beam and not quantum state-selected as was done by van den Brom *et al.*

Timing Resolution of the PImMS1 Sensor

To characterize the time-resolution of both our VMI instrument and the PImMS1 sensor, the CO fragment in the $J = 59$ quantum state was also probed. The CO($J = 59$) fragment was ionized at 229.89 nm, which, as mentioned earlier, leads to a highly anisotropic distribution ($\beta \sim 1.5$) that has a pronounced node in the Newton sphere. By probing the CO fragments with the polarization vector of the photolysis light perpendicular to the detector plane (‘perpendicular polarization’), the node can be recorded in one or more time-resolved PImMS1 sliced images. The time-resolution of the measurements will be revealed by comparison to simulated data that have a convolution applied in the ToF coordinate.

Figure 3.6(a) shows the simulated ToF profile for CO($J = 59$) fragments generated perpendicular to the detector plane (green solid line) without any convolution applied to the data. The node is clearly seen as a decrease in signal around the centre of the ToF profile, while the same feature is less well-resolved in the corresponding experimental

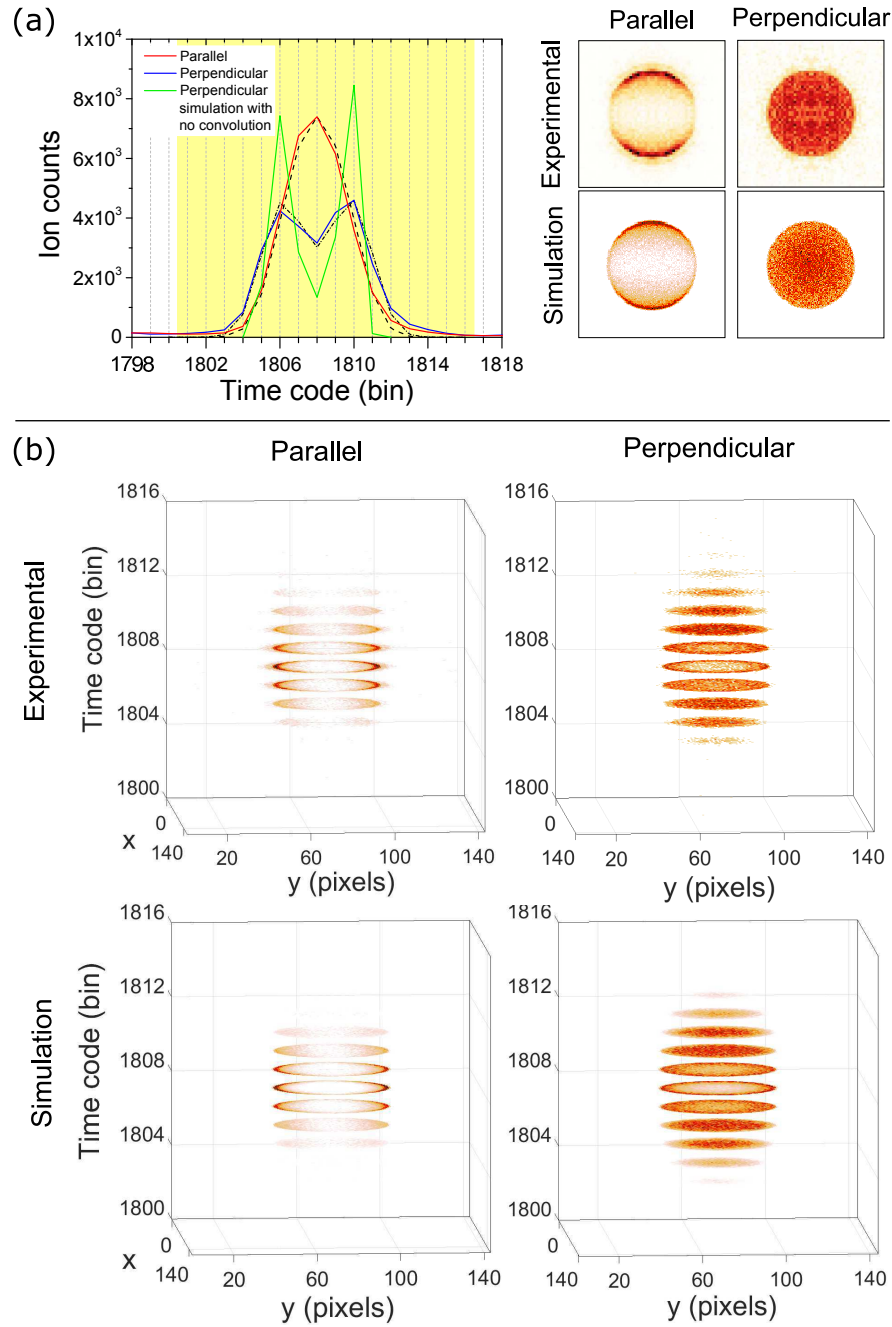


Figure 3.6: Images of CO photofragments produced following the photodissociation of OCS at 229.90 nm probing the $J = 59$ rotational quantum state, and recorded with the PImMS1 camera. Panel (a): The left hand panel shows the ToF peak of CO^+ ions obtained with parallel (solid red line) and perpendicularly (solid blue line) polarized light. The yellow shading in the ToF graph shows the range of time codes that were considered. The corresponding simulated data with a 25 ns convolution applied (black dotted trace) are shown for both configurations. In the perpendicular case, the simulated data without a convolution (green solid trace) is also shown. The two centroided crushed ion images from experiment and simulation (right panels) are shown for each laser polarization. Panel (b): The set of corresponding experimental and simulated 4D plots obtained in the two polarizations (as indicated).

profile (blue solid line), with a less pronounced dip in signal around the centre of the distribution. Applying a convolution of ~ 25 ns to the simulated data along the ToF coordinate leads to a near-perfect match between the experimental (blue solid line) and the convoluted simulated (black dashed trace) ToF profiles.

In the same measurement, the parallel geometry was recorded simultaneously using a photoelastic modulator (PEM) by switching the polarization of the photolysis laser between parallel and perpendicular to the detector plane on alternate laser shots. The ToF profile for the parallel configuration (red solid line) also has a near-perfect match with its corresponding convoluted simulated profile (black dashed trace). A good match is also seen between the experimental and simulated crushed ion images shown in the right hand inset of Figure 3.6(a), for both parallel and perpendicular geometries. Figure 3.6(b) shows an excellent agreement between the 4D plots of the experimental and convoluted simulated sliced images. From the 4D plots, a $\cos^2 \theta$ angular distribution of photofragments is clearly seen, with a large positive β value of 1.64 ± 0.04 extracted from the corresponding central slice in the parallel geometry. Although a smaller β value of 1.55 ± 0.04 was obtained from the reconstructed slice image, both agree with the previously reported value of 1.51 ± 0.09 by van den Brom *et al.* for the dissociation of state-selected OCS [195].

The total ToF resolution, σ_{tot} , is composed of several contributions to the experimental response time of our instrument, which include: the PImMS1 sensor (σ_{P1}), the scintillator screen response (σ_{sc}), the longitudinal velocity of the molecular beam (σ_{MB}), the convolution of two points in the finite interaction region (σ_{int}), the effects of the laser pulse width (σ_{YAG}), and the time-resolution of the MCPs (σ_{MCP}), according to

$$\sigma_{\text{total}} = \sqrt{\sigma_{\text{P1}}^2 + \sigma_{\text{sc}}^2 + \sigma_{\text{MB}}^2 + \sigma_{\text{int}}^2 + \sigma_{\text{YAG}}^2 + \sigma_{\text{MCP}}^2} \quad (3.6)$$

The time-resolution of the MCPs is < 100 ps [231], whilst the time-resolution of the photolysis laser was limited by the laser temporal width of the Nd:YAG Continuum II laser which was 4-6 ns.

The contributions from the molecular beam valve and the finite interaction region were determined through SIMION ion trajectory simulations [173]. In the former, the

calculated mean speed of a molecular beam consisting of 10% OCS seeded in Helium was 1227 m s^{-1} with a spread of 52 m s^{-1} . A 2 ns difference in the ToF was extracted from a particle with an initial beam velocity of either 1227 m s^{-1} or 1278 m s^{-1} . In the finite interaction case, two simulations with 5000 trajectories each were carried out with initial starting positions that were offset by $50 \mu\text{m}$ from either side of the centre of the interaction region. The ToF difference between the two starting positions was 1.4 ns. The P47 phosphor scintillator screen has a rise time of $6.7 \pm 0.2 \text{ ns}$ [232] leading to a σ_{sc} of 3.1 ns.

Since these five parameters have a relatively small contribution to the total ToF resolution in the presence of the PImMS camera, they are grouped together as the ‘rest’ of the contribution, σ_{r} , given by

$$\sigma_{\text{r}} = \sqrt{\sigma_{\text{sc}}^2 + \sigma_{\text{MB}}^2 + \sigma_{\text{int}}^2 + \sigma_{\text{YAG}}^2 + \sigma_{\text{MCP}}^2} \quad (3.7)$$

with an estimated value of 5.6-7.2 ns to give

$$\sigma_{\text{tot}} = \sqrt{\sigma_{\text{P1}}^2 + \sigma_{\text{r}}^2}. \quad (3.8)$$

By rearranging Equation (3.8), the ToF resolution of the PImMS1 sensor is described by

$$\sigma_{\text{P1}} = \sqrt{\sigma_{\text{tot}}^2 - \sigma_{\text{r}}^2}. \quad (3.9)$$

The value of $\sigma_{\text{tot}} \sim 25 \text{ ns}$ leads to a σ_{P1} value of $\sim 24 \text{ ns}$. In work carried out by Michael Burt at the same repeller voltage of 1 kV that the data presented in this chapter were recorded at, the σ_{P1} value was determined to be $20.0 \pm 3.6 \text{ ns}$, and is in agreement with the value of $\sim 24 \text{ ns}$. At 1 kV, the ToF resolution for the rest of the instrument, σ_{r} , was determined to be 7 ns when using the P47 phosphor screen which also agrees with the estimated value of 5.6-7.2 ns. In summary, at a repeller voltage of 1 kV, the instrument has a time-resolution of $\sim 7 \text{ ns}$, and the time-resolution of the PImMS1 sensor was determined to be ~ 20 -25 ns corresponding to approximately two PImMS1 time bins.

3.3.4 The $S(^1D_2)$ Photofragment

It is well known from literature that the $S(^1D_2)$ fragment is generated with two broad KERs following the photodissociation and (2+1) REMPI of OCS at 230.01 nm [114, 187, 192]. In the following section, data is presented to illustrate how nested Newton spheres with broad features are recorded with the PImMS1 sensor.

3D Sliced Images

The ToF distribution of the $S(^1D_2)$ fragment is shown on the left hand panel of Figure 3.7(a). The centroided crushed, symmetrised slice and pBasex ion images are shown on the right hand inset. The individual sliced images shown in panel (b) were recorded

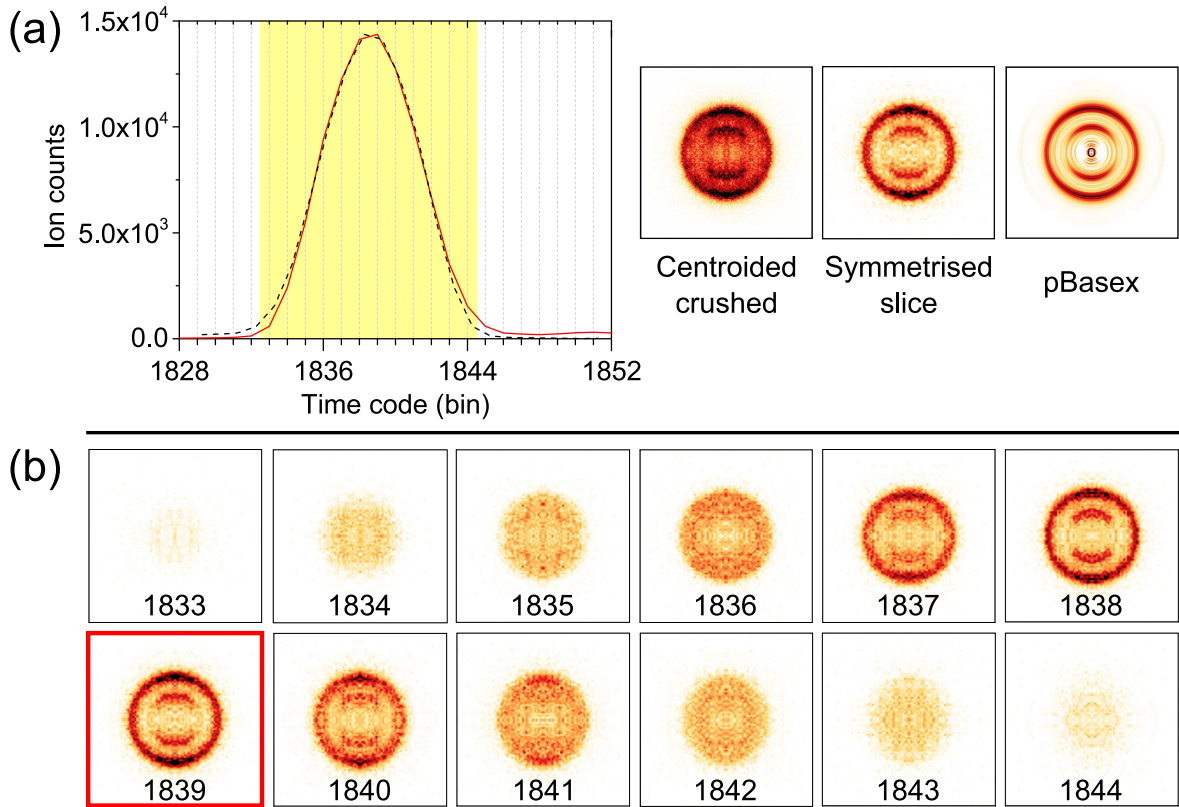


Figure 3.7: Similar to Figure 3.3, but showing images of $S(^1D_2)$ photofragments produced following the photodissociation of OCS at 230.01 nm, recorded using the PImMS1 camera. Panel (a): The left panel shows the ToF peak of S^+ ions (solid red line). The same peak is also shown reflected around the line center (broken black line). The yellow shading in the ToF graph shows the range of time codes that were considered. Each number indicates the time bin of the slice image. The three ion images shown on the right are (from left): the centroided crushed image, the centroided symmetrized central slice image, and the pBasex-inverted images. Panel (b): The images corresponding to the individual time slices as indicated.

with a slicing resolution of 8%. The corresponding 4D plot of these sliced images in Figure 3.5(c) clearly shows that two nested Newton spheres have been successfully recorded with the PImMS1 sensor.

The $S(^1D_2)$ speed distributions are shown in Figure 3.4(b) for the symmetrised central slice and Abel inverted crushed image. They agree well with each other, and with the previously reported speed distribution by Brouard and coworkers [200]. The bimodal speed distribution of the $S(^1D_2)$ fragment is a direct consequence of the bimodal rotational distribution that the CO cofragment is born with. As mentioned earlier in Section 3.3.1, rotationally hot CO cofragments lead to a small KER in the sulphur atoms (inner Newton sphere), whilst rotationally cold CO cofragments are partnered with the fast sulphur atoms (outer Newton sphere).

The β Parameter

The β parameter for the fast, β_{fast} , and slow, β_{slow} , $S(^1D_2)$ fragments were extracted from both the central slice and Abel-inverted crushed image. A β_{fast} value of 0.25 ± 0.08 and 0.31 ± 0.04 were extracted from the central slice and Abel-inverted image, respectively, while a β_{slow} was determined to be 1.09 ± 0.010 and 1.05 ± 0.05 from the two respective images. The β_{fast} and β_{slow} values from the PImMS1 central slice are compared to previously reported measurements in Table 3.1.

The β_{fast} value agrees, within the error bars, with the value of 0.3 reported by van den Brom *et al.* [195] in the dissociation of state-selected OCS at 230 nm. Our value

	288 nm	248 nm	230 nm*	230 nm	223 nm	193 nm
	[197]	[200]		[195]	[189]	[233]
β_{slow}	—	0.73	1.09	1.6	1.8	0.8
β_{fast}	-0.70	-0.02	0.25	0.3	0.7	0.4

Table 3.1: Average spatial anisotropy parameters, β , for fast and slow $S(^1D_2)$ photofragments at a range of wavelengths within the first absorption band of OCS. The β value from this work is indicated by the star, and was obtained from the central slice of the PImMS data set. Note that Zare and coworkers reported a value of $\beta_{\text{fast}} = 0.20$ following dissociation at 223 nm [190]. The values at 223 nm are also similar to the average of those determined by Houston and coworkers using Doppler-resolved LIF of the CO photofragments. [186]

also agrees within error with the value of 0.20 reported by Zare and coworkers [190] in the dissociation of OCS at 223 nm. The β_{slow} value from this work shows a relatively large discrepancy with literature. One reason for the lower anisotropy of slow S atoms in our data as compared to Ref. [195] is that the $\text{S}(^1\text{D}_2)$ photofragments are born highly polarized in the photodissociation of OCS, and no correction has been attempted in this work to account for the effects of S-atom electronic angular momentum polarization.

3.3.5 Comparison of Cameras

In this section, the PImMS1 camera is compared to a conventional intensified CCD camera, followed by a comparison between PImMS1 and PImMS2.

Comparison of PImMS1 with a CCD Camera

A comparison is made here between the PImMS1 camera (obtained by summing the complete set of slices through the 3D scattering distribution) and a conventional time-gated CCD camera by extracting the reconstructed central slice from the pBasex-inversion [213] of their respective crushed images. Figure 3.8 presents data recorded with both cameras for the (a) $\text{CO}(J = 46)$ and (b) $\text{S}(^1\text{D}_2)$ fragments following the one-colour photodissociation of OCS at around 230 nm. For both fragments, the first two panels present the crushed and corresponding pBasex-inverted ion images recorded with the PImMS1 and CCD cameras, whilst the third image shows a comparison between the two reconstructed images.

There is a good qualitative match between the ion images shown for the two cameras. A quantitative comparison between both reconstructed images is made through their speed and angular distributions, which show a good agreement. It is striking to see that the reduced pixel array in the PImMS1 sensor (72×72 pixels) can record comparable ion images to a CCD camera (576×768 pixels), since the latter has ~ 85 times more pixels than the former. In the case of the $\text{S}(^1\text{D}_2)$ photofragment, the resolution obtained with PImMS is better.

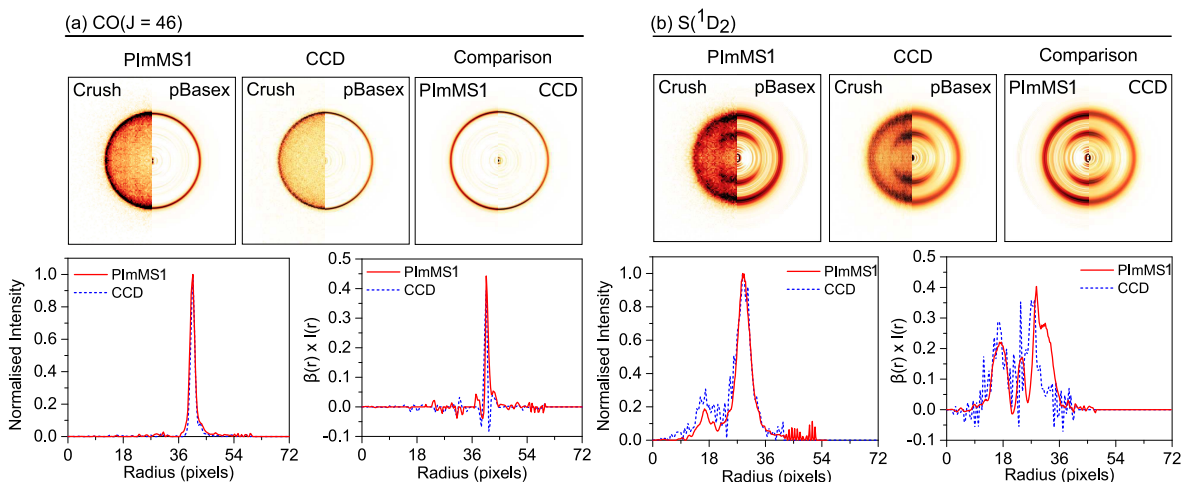


Figure 3.8: A comparison of the ion images recorded using the PImMS1 camera and a conventional CCD camera following the photodissociation of OCS at (a) 229.98 nm and (b) 230.01 nm. In each panel, going from left to right, the three images presented are those recorded using the PImMS1 camera, the conventional CCD camera, and a comparison of the pBasex inverted images collected using the two cameras, as labelled. Beneath the images are the corresponding speed (left) and weighted β parameters (right), extracted using the pBasex image inversion algorithm. Errors in the speed distributions obtained directly from the central slice are typically around 5% at the peak of the distribution.

Comparison of PImMS1 and PImMS2 Sensors

The crushed ion images recorded with the PImMS1 and PImMS2 cameras are shown in Figure 3.9 for the (a) CO($J = 46$), (b) CO($J = 59$), and (c) S(1D_2) fragments following the one-colour photodissociation of OCS at around 230 nm. Both sets of data were megacentroided, binned into a pixel array twice the original sensor dimensions (*i.e.* PImMS1: 144×144 pixels; PImMS2: 648×648 pixels), and subsequently four-fold symmetrized to improve the signal-to-noise in the ion images.

Although the ion images recorded with the PImMS2 camera have significantly better resolution, the relevant features in the ion images recorded with the PImMS1 camera are still resolved for all three fragments. This is particularly impressive since the former has ~ 20 times more pixels to detect an event than the latter. It should be noted that the ion images for the CO($J = 59$) fragment show the most noticeable difference between the two sensors, with the existence of two distinct and well-resolved KER channels in the PImMS2 image which correspond to the $v = 0$ and $v = 1$ vibrational quantum levels of the parent molecule. These features are partially resolved in the PImMS1

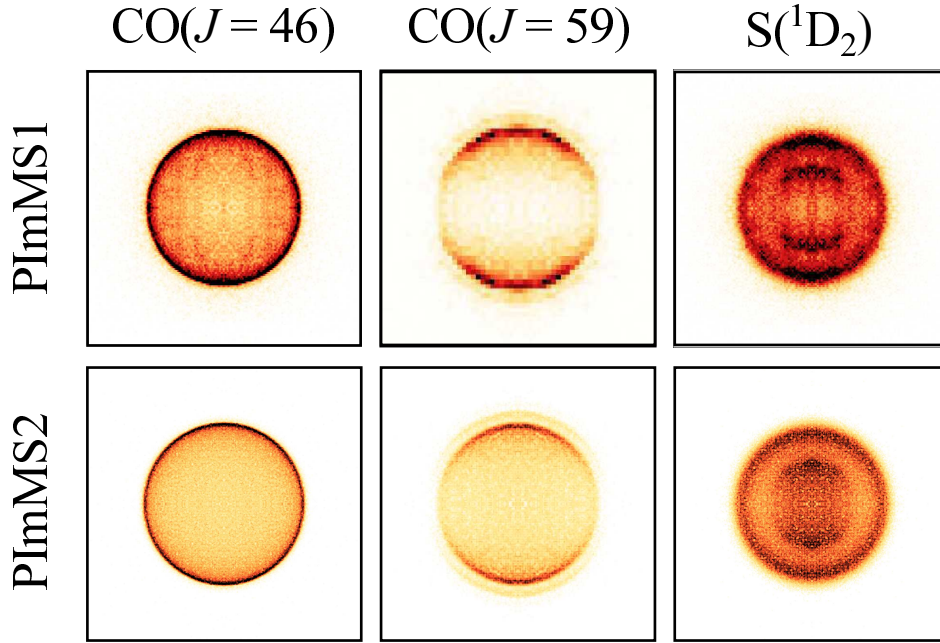


Figure 3.9: A comparison of crushed ion images recorded with the PImMS1 (top row) and the PImMS2 (bottom row) cameras, for $\text{CO}(J = 46)$, $\text{CO}(J = 59)$, and $\text{S}(^1D_2)$ fragments following the photodissociation of OCS at 229.98 nm, 229.88 nm and 230.01 nm, respectively.

case.

Figure 3.10 shows the crushed and reconstructed central slice images for the $\text{CO}(J = 46)$ and $\text{S}(^1D_2)$ fragments in panels (a) and (b), respectively. Although the PImMS1 crushed image is not as well resolved as the PImMS2 image, both generate comparable pBasex-inverted slice images. Their corresponding speed and angular distributions also show an excellent quantitative agreement between the both cameras.

The central slices recorded by the PImMS2 camera for all three fragments are shown in Figure 3.11 before and after symmetrisation (first two columns), with an improvement in signal-to-noise generated in the latter. Although the symmetrised slice image (middle column) compares well to the corresponding reconstructed ion image (last column), the latter contains both noise and artefacts that arise from the Abel-inversion process.

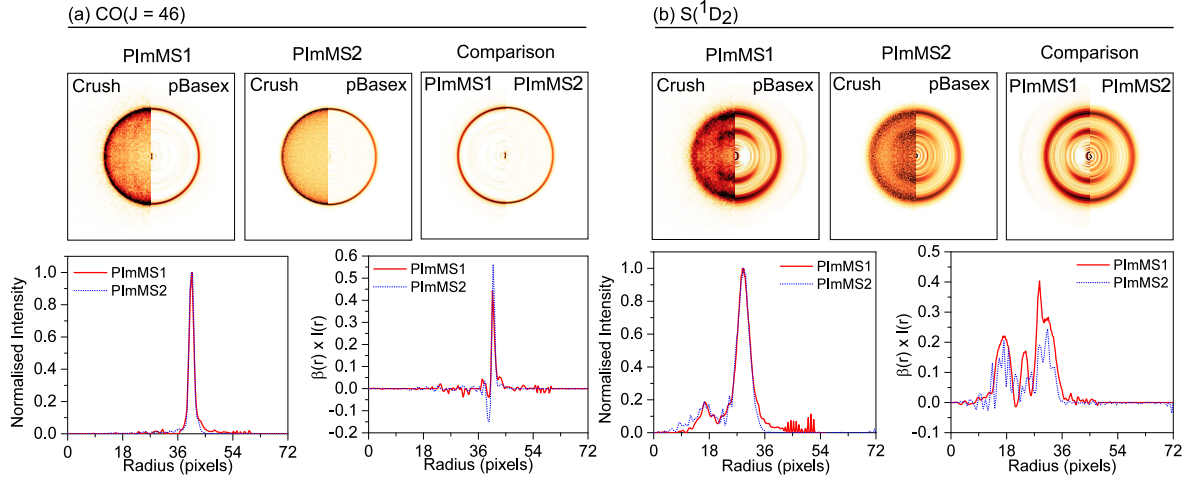


Figure 3.10: A comparison of the ion images recorded using the PImMS1 camera and the PImMS2 camera following the photodissociation of OCS at (a) 229.98 nm and (b) 230.01 nm. In each panel, going from left to right, the three images presented are those recorded using the the PImMS1 camera, the PImMS2 camera, and a comparison of the pBasex inverted images collected using the two cameras, as labelled. Beneath the images are the corresponding speed (left) and weighted β parameters (right), extracted using the pBasex image inversion algorithm. Errors in the speed distributions obtained directly from the central slice are typically around 5% at the peak of the distribution.

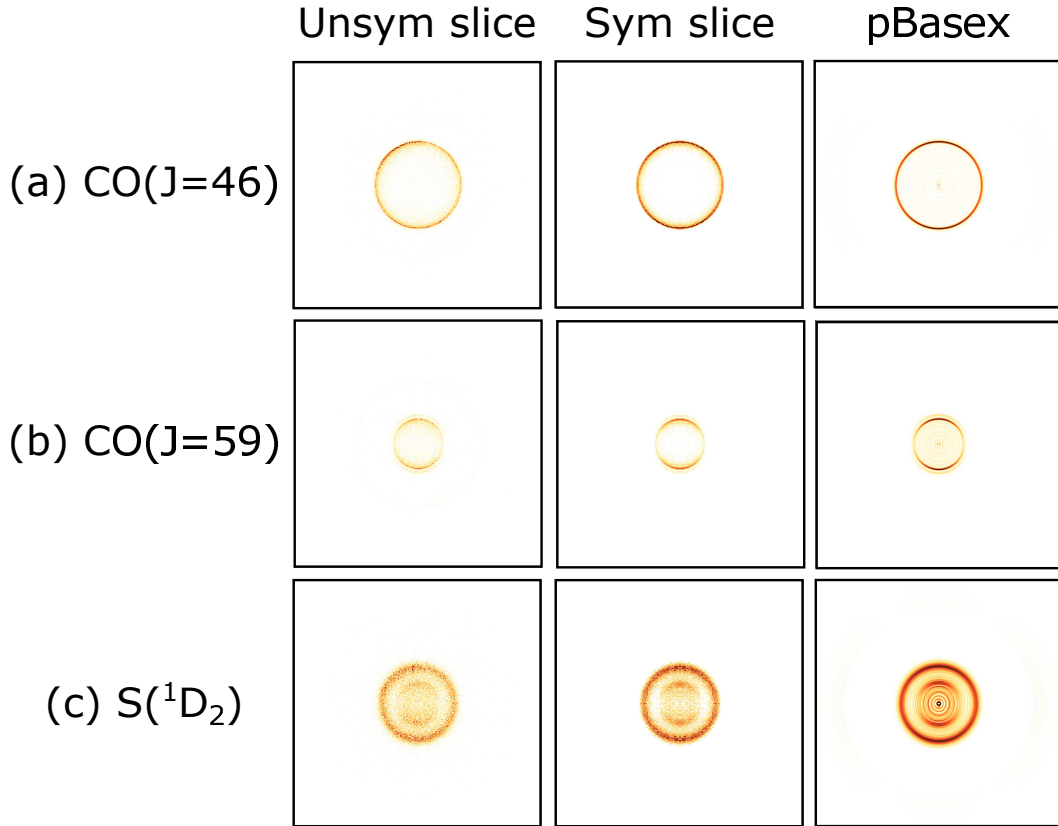


Figure 3.11: Slice ion images of the (a) CO($J = 46$), (b) CO($J = 59$), and (c) S(1D_2) fragments recorded with the PImMS2 camera following the photodissociation of OCS at ~ 230 nm. The three columns of ion images correspond to the pre- and post-symmetrized centroided central slice, and the pBasex-inverted image.

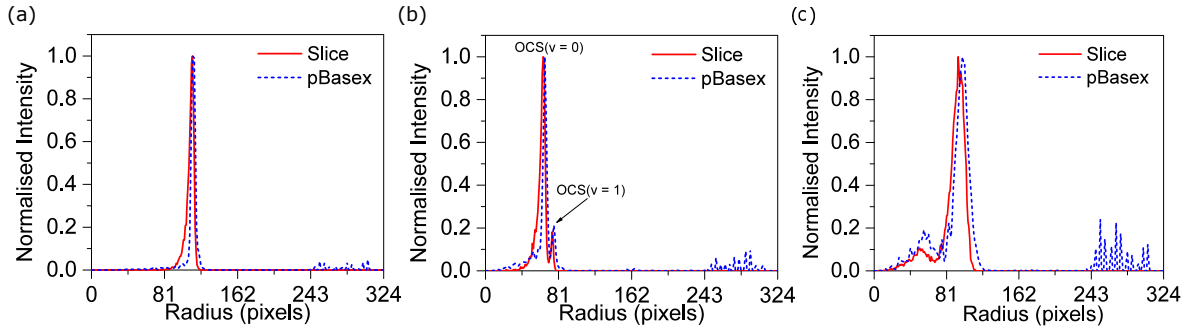


Figure 3.12: The speed distribution extracted from the PImMS2 central slice (red continuous line) and the pBasex slice (blue dashed line) for (a) the CO($J = 46$), (b) CO($J = 59$) and (c) the S(1D_2) photofragments following the one colour molecular photodissociation of OCS at 229.98 nm, 229.90 nm and 230.01 nm, respectively. Errors in the experimental PImMS2 data are typically around 5% at the peak of the distribution

Very good agreement is seen in the corresponding speed distributions from the PImMS2 slice (red continuous line) and pBasex slice (blue dashed line) images, shown in Figure 3.12, for all three fragments. The speed distribution for the pBasex slice is slightly narrower and is shifted to faster speeds due to the pBasex algorithm generating an infinitesimally small slice in time out of the centre of the reconstructed distribution of ions, leading to the highest velocity resolution for this measurement. The PImMS2 camera records a slice with a relatively large bin width of 12.5 ns, and so leads to a slightly larger velocity resolution. Two distinct KER channels exist in the speed distribution of the CO($J = 59$) fragment as seen in its ion images, corresponding to the ground and first excited vibrational state of the parent molecule.

The β parameter was extracted from the PImMS1 and PImMS2 slices and pBasex ion images for all three fragments, and is shown in Table 3.2. These values are also

	CO($J = 46$)	CO($J = 59$)	Slow S(1D_2)	Fast S(1D_2)
PImMS1 slice	0.311 ± 0.005	1.640 ± 0.040	1.090 ± 0.010	0.250 ± 0.080
PImMS2 slice	0.367 ± 0.021	1.460 ± 0.025	1.120 ± 0.010	0.363 ± 0.040
PImMS1 pBasex	0.259 ± 0.021	1.550 ± 0.040	0.310 ± 0.040	0.310 ± 0.040
PImMS2 pBasex	0.207 ± 0.017	1.030 ± 0.030	0.617 ± 0.080	0.255 ± 0.033
Literature [195]	0.370 ± 0.050	1.510 ± 0.090	1.6	0.2

Table 3.2: The spatial anisotropy parameter, β , extracted from the PImMS1 and PImMS2 sliced and pBasex ion images for the CO($J = 46$), CO($J = 59$), and the slow and fast S(1D_2) fragments following the one-colour photodissociation and ionization of OCS at ~ 230 nm. Literature values are also shown from the photodissociation of state-selected OCS at 230 nm by van den Brom *et al.* [195].

compared to their corresponding literature values from the photodissociation of state-selected OCS at 230 nm by van den Brom *et al.* [195]. In the CO($J = 46$) fragment, only the PImMS2 slice data (0.367 ± 0.021) is in agreement with its corresponding literature value (0.370 ± 0.050). While in the CO($J = 59$) fragment, both slice data and the PImMS1 pBasex data agree with their corresponding literature value, with the best agreement seen with the latter.

In the S(1D_2) fragments, only the PImMS1 slice (0.250 ± 0.080) for the fast fragments is in agreement with its corresponding literature value (0.2). As mentioned previously, the discrepancy between the β values from literature and the PImMS data for the S(1D_2) fragments could reflect the fact that the latter was not corrected for the effects of S-atom electronic angular momentum polarization. In general, Table 3.2 has shown that the PImMS slices have an overall better agreement with their corresponding literature values than in the pBasex case. It clearly shows the advantages of directly recording the full 3D distribution of ions, and therefore bypassing reconstruction algorithms and their inherent introduction of noise and artefacts.

3.4 Simulations

This section presents the optimization of the DC slice imaging set-up [142] using SIMION [173] trajectory simulations, and the details of the steps used to simulate the experimental data that were presented earlier in this chapter.

3.4.1 Optimization of DC Slice Imaging Set-Up

An ion trajectory simulation of the DC slice imaging set-up [142], using SIMION 8.1, was carried out, with the 3D potential energy view of the configuration shown in Figure 3.13. Ions are born in the interaction region between the repeller and extractor electrostatic plates (denoted 1 and 2). The ions (white traces) roll down a potential energy hill and are accelerated through the third lens (3) plate, which acts as an electrostatic focusing lens for the charged particles. These ions traverse through the grounded (4) plate and towards the detector.

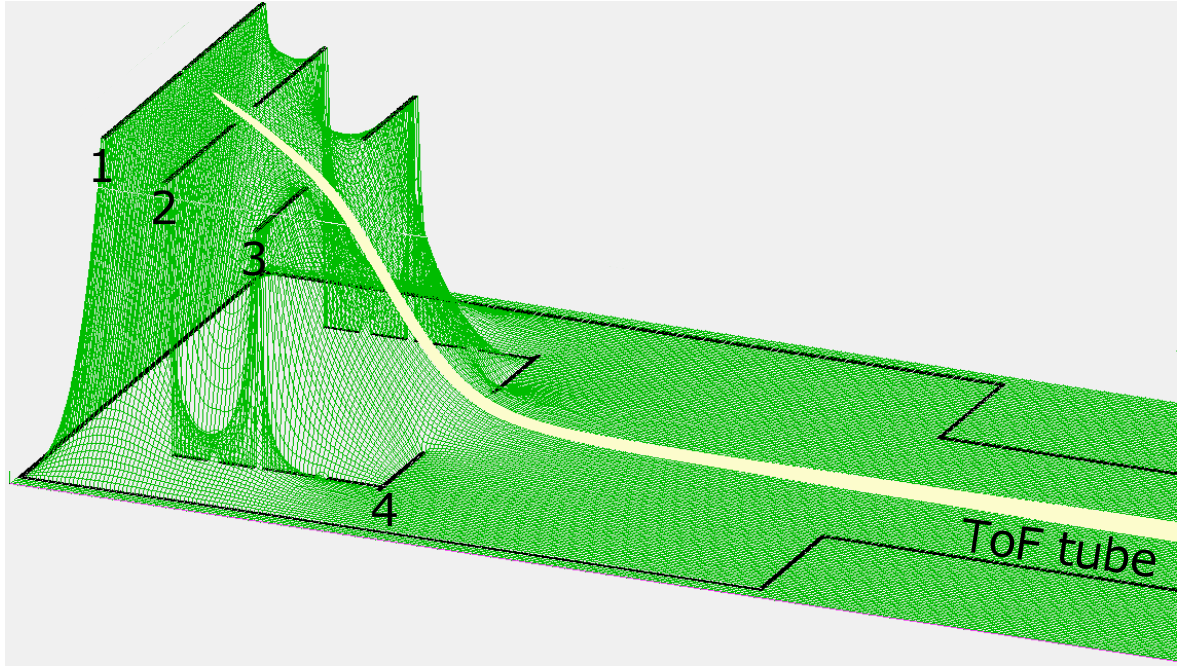


Figure 3.13: Three-dimensional potential energy view of the DC sliced imaging setup simulated using the SIMION 8.1 ion trajectory simulation package. The four electrostatic electrodes used in this design were: the repeller (1), the extractor (2), the third lens (3), and the grounded (4) plates. A field-free region exists between the ground electrode and the detector at the end of the ToF tube.

In the interaction region, a Newton sphere of CO^+ ions is generated in a cylindrical distribution with a length of 0.9 mm and a radius of $53 \mu\text{m}$ to mimic the focal volume of the probe laser. Within this cylindrical volume, ions are born with a Gaussian velocity distribution, with a mean KER of 0.2 eV and a FWHM of 0.02 eV. The settings of the VMI set-up were optimized by flying 5000 ions at various voltage settings. The voltage ratio between the repeller (V_1) and the extractor (V_2) plates, $V_1:V_2$, and the ratio between the repeller and the third lens (V_3), $V_1:V_3$, were varied to determine the optimal voltage settings.

To obtain the best velocity-mapping conditions, a perfect linear correlation is sought between the ions' initial velocities and their arrival-time and position at the detector. The degree of correlation is quantified by the R^2 value [234, 235] which calculates the deviation of the observable value, x_i , from the point that lies on a line of best fit, f_i , and is described by

$$R^2 = 1 - \frac{S_E}{S_T}, \quad (3.10)$$

where S_E is the sum of squares of the regression [234, 235], defined as

$$S_E = \sum_{i=1}^{i=n} (x_i - f_i)^2, \quad (3.11)$$

and S_T is the total sum of squares about the mean [234, 235], defined as

$$S_T = \sum_{i=1}^{i=n} (x_i - \mu)^2, \quad (3.12)$$

where n is the number of ion trajectories, and μ is the mean of the observed data. R^2 can take a value between 0 and 1, with unity representing a perfect fit.

Three parameters were optimized for each voltage setting. Firstly, a correlation of the radius of ion impact with the initial velocity in the plane parallel to the detector (xy-plane), v_{xy} , is determined by calculating the planar R^2 value. Secondly, the time-of-arrival at the detector is correlated to the ion's initial velocity along the ToF axis, v_z , by calculating the ToF R^2 value [235]. Thirdly, the total ToF spread, ΔToF , within the Newton sphere is calculated from the difference between the arrival-time of the first and last ion in the distribution [235]. Figure 3.14 shows examples of excellent and poor correlations in panels (a) and (b), respectively. Here, correlations between the radius of ion impact at the detector, r , and an ion's initial velocity in the detector (xy) plane, v_{xy} , are shown with an R^2 value of 0.9999 and 0.5332, respectively. An R^2 value of above 0.99 is considered good while a value above 0.999 is considered excellent [235].

Figure 3.15 shows the results of varying the extractor voltage (V_2) whilst keeping the voltages on the repeller and third lens fixed ($V_1 = 1000$ V, $V_3 = 775$ V). Panel (a) shows that the ToF R^2 value (*i.e.* the ToF correlation) stays relatively high at all voltage ratios which indicates that a good correlation exists between an ion's ToF and initial velocity in the ToF coordinate (z-axis). In contrast, the correlation between an ion's initial velocity in the detector plane (xy plane) and its radius of impact, given by the 'planar' R^2 value (*i.e.* planar correlation), varies significantly more, with the best correlation found at the $V_1:V_2$ ratio of ~ 0.88 which reaches a maximum planar R^2 value of 1.000. Interestingly, the correlation in the plane of the detector is completely lost at

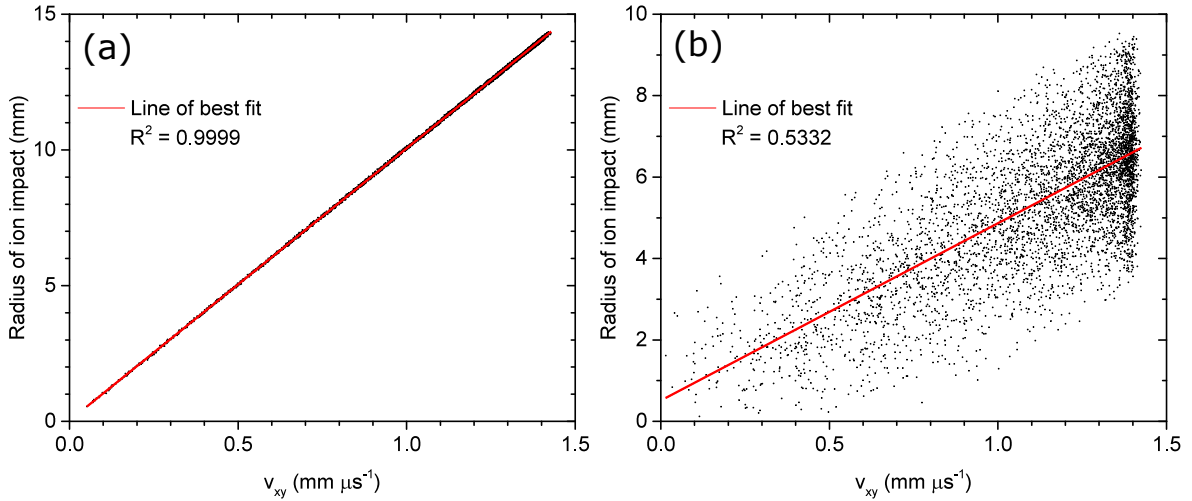


Figure 3.14: Correlation plots of the radius of ion impact at the detector with the ions' initial velocity in the detector (xy) plane is shown for examples of (a) excellent and (b) poor correlations. In each panel, a line of best fit (red solid line) is fitted to the data from which the R^2 value, which quantifies the quality of the fit, can be extracted from.

the $V_1:V_2$ ratio of ~ 0.97 . The most optimal $V_1:V_2$ ratio was determined to be 0.882 as this gave the largest average R^2 value (Spatial $R^2 = 1.0000$ and ToF $R^2 = 0.9997$). At this voltage ratio, a Newton sphere of ions is generated with a total ToF spread that spans 9 PImMS time bins as shown in Figure 3.15(b).

The $V_1:V_3$ ratio was then optimized by varying V_3 whilst keeping V_1 and V_2 fixed at 1000 V and 0.882 V, respectively. The results of this optimization are shown in Figure

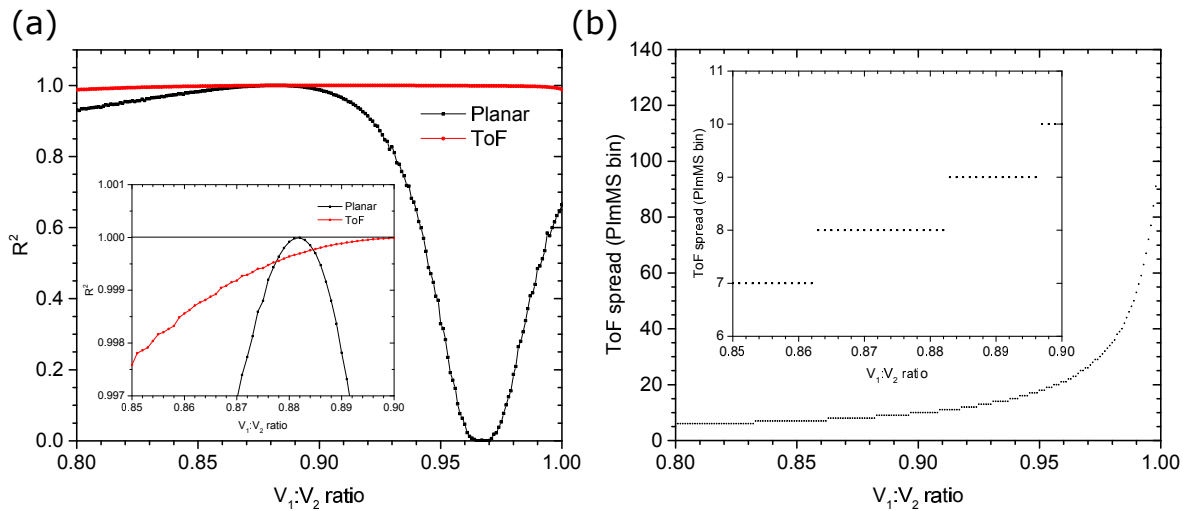


Figure 3.15: (a) Planar (black) and ToF (red) R^2 values plotted as a function of $V_1:V_2$ voltage ratio. The inset shows a zoom-in of the R^2 values between the voltage ratio of 0.80 and 0.90 where the best correlation exists. (b) The ToF spread of the Newton sphere of ions at each $V_1:V_2$ voltage ratio. The inset shows a zoom-in of the ToF spread around the voltage ratio which gives the best ToF and planar R^2 values.

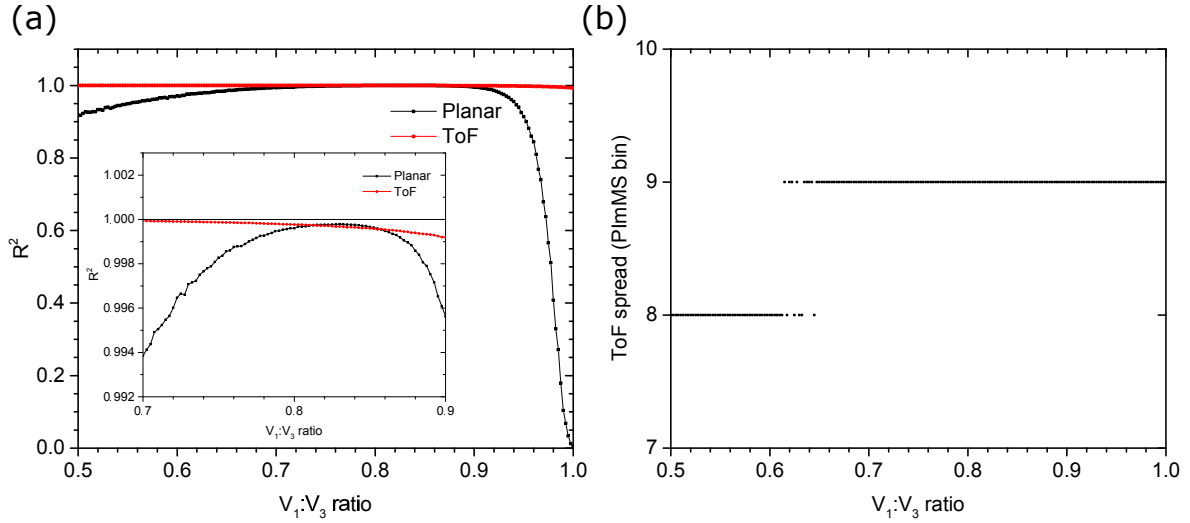


Figure 3.16: (a) Planar (black) and ToF (red) R^2 values plotted as a function of $V_1:V_3$ voltage ratio. The inset shows a zoom-in of the R^2 values between the voltage ratio of 0.70 and 0.90 where the best correlation exists. (b) The ToF spread of the Newton sphere of ions at each $V_1:V_3$ voltage ratio.

3.16. The R^2 value for the ToF correlation stays above 0.99 throughout, while the planar correlation varies much more significantly, with a maximum at a $V_1:V_3$ ratio of 0.830. The optimal $V_1:V_3$ ratio was determined to be 0.815 (spatial $R^2 = 0.9998$ and ToF $R^2 = 0.9997$). At this optimal $V_1:V_3$ ratio, a Newton sphere of ions was generated that spanned a total of 9 PImMS time bins as shown in Figure 3.16(b). In conclusion, the optimal $V_1:V_2:V_3$ voltage ratio was determined to be 1.000:0.882:0.815, which is slightly different to the experimentally determined ratio of 1.000:0.886:0.775. Although there is a discrepancy in the third lens voltage between simulation and experiments, one can see from Figure 3.16 that the $V_1:V_3$ ratio of 0.775 still gives good ToF and planar correlations.

3.4.2 Simulation of Experimental Results

With prior knowledge of the β parameter for photolysis of OCS at 230 nm, the Newton sphere of ions was simulated using a Gaussian velocity distribution. The mean KER of the fragment ions was determined by calculating the total energy available, E_{avl} , in the OCS molecule after the absorption of a photon, $E_{h\nu}$, which is given by

$$E_{\text{avl}} = E_{h\nu} - D_0 \quad (3.13)$$

where D_0 is the dissociation energy to yield $S(^1D_2) + CO$ products, and has a value of 4.291 eV [199]. The total available energy is also equal to the sum of the product translational energy and the CO internal excitation as given by

$$E_{\text{avl}} = E'_{\text{trans}} + E'_{\text{rot}} + E'_{\text{vib}}. \quad (3.14)$$

Since the CO photofragments are generated in their vibrational ground state [186, 189], it is assumed that $E'_{\text{vib}} \approx 0$. The rotational energy of the CO fragment is given by

$$E'_{\text{rot}} = B J(J + 1) \quad (3.15)$$

where B is the rotational constant with a value of 1.93128 cm^{-1} for CO [236] and J is the rotational quantum number. The product translational energy is given by

$$E'_{\text{trans}} = \frac{1}{2} \mu \nu_{\text{rel}}^2 \quad (3.16)$$

where ν_{rel} is the sum of the relative product velocity and μ is the reduced mass. Combining equations 3.14 and 3.16 leads to

$$\nu_{\text{rel}} = \sqrt{\frac{2(E_{\text{avl}} - E'_{\text{rot}})}{\mu}}. \quad (3.17)$$

The velocity of the CO fragment was determined using linear momentum conservation, and was subsequently used as the mean of the Gaussian initial kinetic energy distribution in the SIMION simulations.

In the simulation of the $CO(J = 46)$ fragment, CO^+ ions were generated with a mean KER of 0.317 eV. With prior knowledge of the β parameter, ions were flown towards the detector only if their angular distribution, given by Equation (3.4), were greater than a randomly generated number. The resulting distribution $I(x, y, t)$ of ion arrival positions and times were binned into a 144×144 pixel array in 12.5 ns steps in the same way as the experimental data.

The simulated ToF (black solid line) is shown in the left panel of Figure 3.17 for

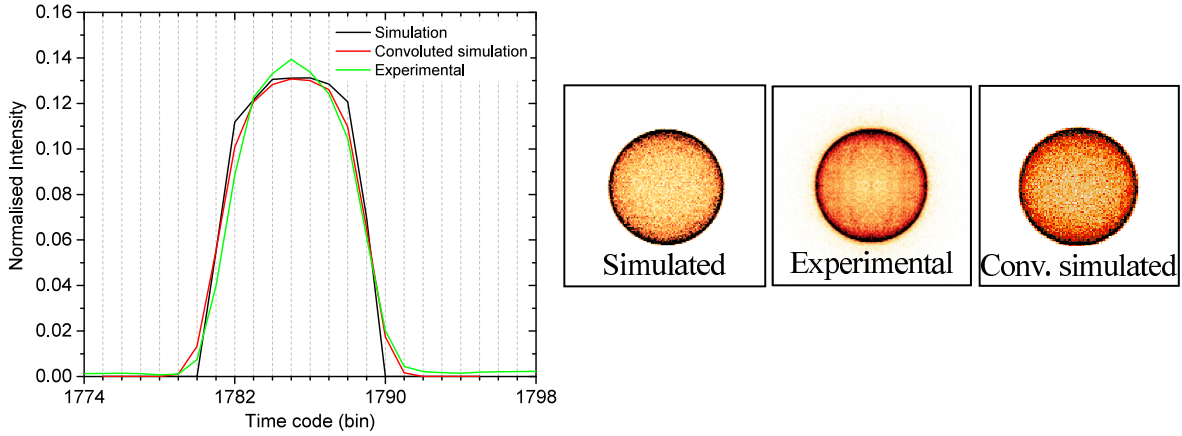


Figure 3.17: The ToF profile of $\text{CO}(J = 46)$ photofragments from experimental (green line) and simulated data with (red line) and without (black line) a convolution in the ToF coordinate. The corresponding crushed ion images are presented in the right panel.

$\text{CO}(J = 46)$ fragments. The simulated ToF profile spans 9 time bins which is two fewer than in the experimental (green solid line) ToF profile. The latter contains a fairly symmetric ToF profile with a pronounced peak whilst the simulation shows a flatter maximum. The corresponding crushed ion images are presented in the right hand panel of Figure 3.17, with no significant differences seen between the simulated and experimental ion images.

The individual sliced images corresponding to each time bin are plotted on top of each other to generate a four-dimensional (x, y, t, I) intensity plot of the Newton sphere of ions as shown in Figure 3.18. The subtle differences seen in the ToF profiles now appear even more pronounced in the 4D plots. The simulated 3D distribution of ions in panel (a) contain a near-perfect spherical distribution. However, the experimental distribution, shown in panel (b), is elongated along the time axis. The discrepancy is due to the fact that the perfect simulation case does not take into account the experimental response time of the instrument (including the effects of the laser pulse width, phosphor response, and camera response time) [183, 232].

Convoluting the simulated distribution of ions with a Gaussian of full-width-half-maximum ~ 25 ns in the time domain gave the 4D distribution shown in panel (c), which agrees well with the corresponding experimental distribution shown in panel (b). The corresponding ToF profile for the convoluted simulated data (red solid trace) is shown in Figure 3.17. The ToF profile now spans the same number of time bins (11

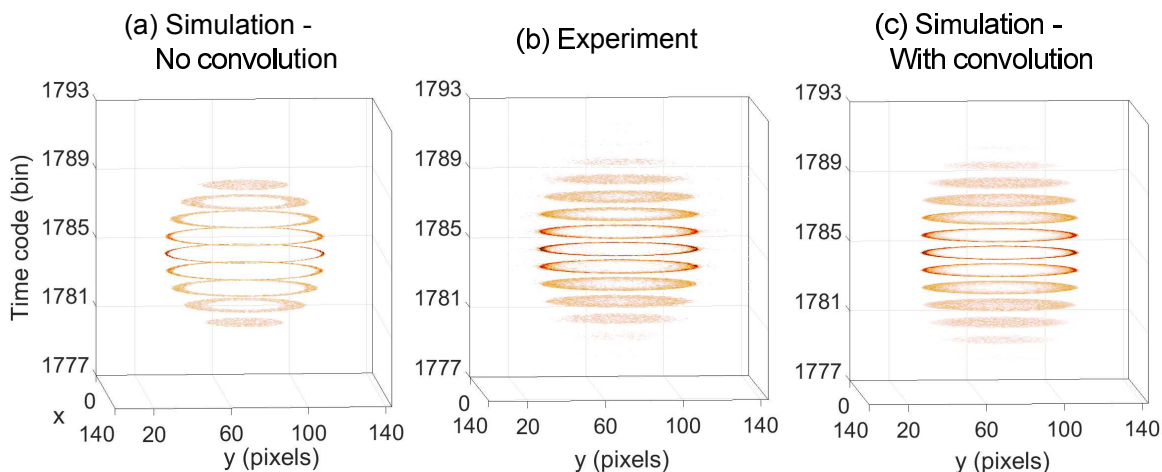


Figure 3.18: 4D plots of (a) the simulated and (b) experimental Newton spheres for the $\text{CO}(J = 46)$ photofragment, and (c) the simulated Newton sphere for the same fragment but with a convolution to simulated data in the ToF coordinate. The experimental data were obtained subsequent to the one colour molecular photodissociation of OCS at 229.98 nm.

time bins) as the experimental distribution (green solid trace).

3.5 Conclusions

This chapter demonstrated that the PImMS1 camera has successfully recorded the full 3D distribution of ions generated from the one-colour photodissociation and subsequent (2+1) REMPI detection of OCS at around 230 nm. The PImMS1 camera was coupled with a standard MCP-phosphor screen detector and a conventional DC sliced imaging set-up to record the x - and y -position as well as the arrival-time of a particle. Time-resolved slices through the Newton sphere of ions were recorded with a timing precision of 12.5 ns and a time-resolution of ~ 20 –25 ns. The latter was determined by a comparison of the experimental data to simulated data convoluted in the ToF coordinate. The convolution took into account the experimental response time of the DC sliced imaging instrument which includes contributions from the laser pulse width, the phosphor screen response time, and the PImMS1 camera response time.

The speed distributions recorded by both PImMS1 and PImMS2 cameras have a velocity resolution of 6–9%, which matches the simulated data well. This was aided by the use of a centroiding algorithm based on the arrival-time of ions which generates a single accurate position and arrival-time for each ion [54, 56, 114, 183].

The data was subsequently binned into a “virtual” pixel array twice the original sensor dimensions through the method of mega-centroiding (*i.e.* PImMS1: 144×144 pixels; PImMS2: 648×648 pixels) leading to an improvement in both the spatial precision and resolution of our data.

Up to 11 time-resolved slices were recorded through the Newton sphere giving a slicing resolution of ~ 0.09 . The optimization of the DC slice imaging set-up using SIMION 8.1 [173] ion trajectory simulations showed that the slicing resolution could not be further improved under good velocity-mapping conditions, with the largest ToF spread in the Newton sphere already achieved in the experimental results that were presented. To improve the slicing resolution of our experiment, a larger ToF spread in the Newton sphere under good velocity-mapping conditions must be achieved since the timing precision of the PImMS slices cannot currently be reduced below 12.5 ns.

In summary, the 3D imaging capability of the PImMS camera has been successfully demonstrated in capturing the Newton sphere of ions (for a one mass-to-charge) generated by a (2+1) REMPI scheme. In the rest of this thesis, the multi-mass capability of the PImMS camera is demonstrated by recording the many ions (with different mass-to-charge ratio) generated from the Coulomb explosion of molecules. The principles of Coulomb explosion imaging are discussed in the following chapter.

Chapter 4

Principles of Coulomb Explosion

Imaging

In this chapter, the principles of Coulomb explosion imaging (CEI) are introduced. A detailed insight into the various photoionization schemes that may induce a Coulomb explosion within a molecule are given. These include non-resonant multiphoton ionization, strong-field ionization, and inner-shell ionization. The latter can trigger one or more relaxation processes that may lead to the ejection of additional electron(s) from the charged particle. Details of the various light sources available to access these ionization schemes are also given. The chapter concludes with an introduction to laser-induced alignment and mixed-field orientation of molecules.

4.1 Background and Motivation

In Coulomb explosion imaging (CEI) [46–62], many electrons are rapidly removed from a target molecule during ionization to generate several charged fragments that contain momentum information on the geometry of the molecule at the time of ionization. The Coulomb explosion process consists of two stages, which are idealized to occur sequentially but, in practice, often happen concurrently. Firstly, several electrons are removed from the target molecule to generate a highly charged molecular ion. This is followed by the Coulomb explosion of the highly charged molecular ion to generate multiple

fragments since the intramolecular Coulomb repulsion far outweighs the binding energy of the highly unstable molecular ion. The fragments are generated with a recoil velocity that is indicative of their starting position in the molecule before ionization.

The first CEI measurements were carried out on simple molecules such as H_2^+ , HeH^+ and CH_4^+ by collision of a fast molecular beam with a thin foil [46–48, 52, 53]. The interaction time between the molecular beam and thin foil was on a timescale short enough (< 1 fs [46–48, 53]) such that the nuclear motion was essentially fixed during the Coulomb explosion process [50].

Femtosecond lasers have unlocked a plethora of opportunities to image a molecules structure, internal bonding, and fragmentation processes [25, 30–33]. The laser-based CEI technique [49, 136] was made possible with high-intensity femtosecond near infrared (NIR) pulses that allow several valence electrons to be rapidly removed from a molecule to generate a highly charged molecular ion that subsequently Coulomb explodes. Structural information about the molecule can be extracted from the resulting recoil velocities of the product ions, which depend on the position of the atoms in the molecule before ionization.

Following a photoinduced chemical reaction, a series of quick snapshots of the non-stationary molecule can be recorded by coupling the laser-based CEI technique with pump-probe experiments. In a pump-probe experiment, as mentioned previously in Chapter 1, the first (“pump”) laser pulse initiates the process of interest, such as the photodissociation of a bond, whilst a second (“probe”) laser pulse ionizes the fragments of interest [49]. By introducing a time delay between the two pulses and recording separate measurements at a series of fixed pump-probe delays, a “molecular movie” of the reaction that was initiated by the pump pulse may be generated. The probe pulse could induce a Coulomb explosion of a molecule through either multiphoton ionization, strong-field ionization or inner-shell ionization, details of which are described in the following sections.

4.2 Ionization by Intense Laser Fields

A single photon from an optical laser typically does not possess enough photon energy to ionize a neutral atom or molecule. Therefore, the process of photoionization may only occur through the absorption of multiple photons, or via significant perturbation of the potential energy barrier binding the electron to the atom or molecule. Non resonant photoionization is often described by one of three regimes: multi-photon, tunnelling, and over-the-barrier ionization, with the latter two falling under the strong-field regime. The dominant photoionization regime can be approximately determined through the Keldysh parameter [237, 238]

$$\gamma = \sqrt{\frac{I_p}{2U_p}}, \quad (4.1)$$

which depends on the ionization potential of the atom or molecule, I_p , and the average kinetic energy of a free electron in an oscillating electric field, given by the ponderomotive potential defined as [239]

$$U_p = 9.337 \times 10^{-20} I_0 \lambda^2, \quad (4.2)$$

where I_0 is the laser intensity and λ is the laser wavelength.

Figure 4.1(a) shows the unperturbed potential of an electron in an atom in the absence of the laser field. The multi-photon regime, shown in Figure 4.1(b), is applied when $\gamma \gg 1$; either the strength of the laser field is much weaker than the Coulombic force of attraction between the electrons and ions, or the time it takes for the electrons to tunnel through the barrier is significantly longer than the period of the oscillating laser field. For increasing laser intensity the strength of the laser field becomes comparable to the Coulombic force of attraction, and ionization is now in the strong-field or tunneling ionization regime with $\gamma < 1$. Here, the Coulombic potential is deformed by the laser field to such an extent that the barrier to ionization is lowered significantly. In tunnelling ionization ($\gamma < 1$), the barrier to ionization has decreased so much so that the electrons can tunnel through the relatively small barrier and out into the continuum as shown in Figure 4.1(c). In over-the-barrier ionization ($\gamma \ll 1$), the magnitude of the

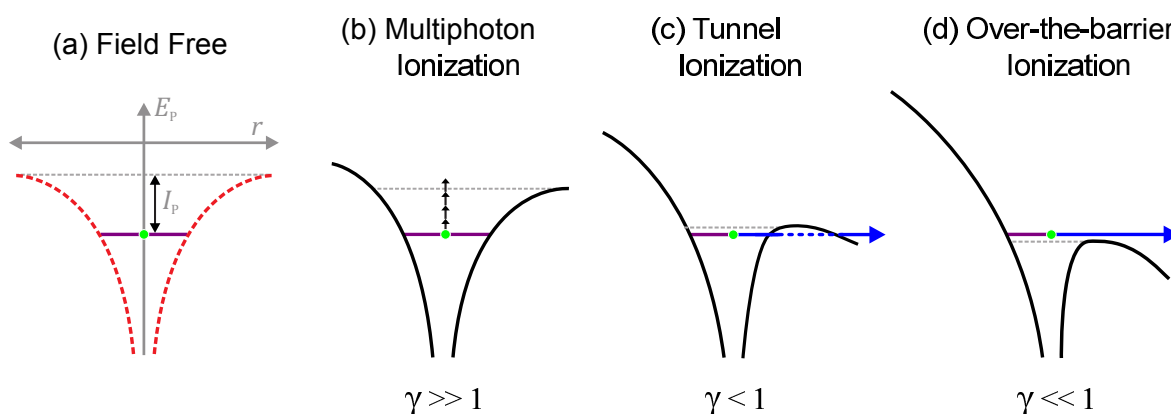


Figure 4.1: The effect of an intense laser field on the atomic Coulomb potential. The (a) field free, (b) multiphoton, (c) tunneling, and (d) over-the-barrier ionization cases are presented. The binding energy is I_p , γ is the Keldysh parameter, E_p is the photon energy, and r is the reaction coordinate. Figure adapted from Reference [145].

laser field is so strong that the deformation of the Coulomb potential leads to a barrier that is below the binding energy of the electrons, with the electrons able to “spill” out into the continuum, as shown in Figure 4.1(d).

If the photon energy is larger than the electron binding energy, one or more electrons may be ejected from the molecule without the need to significantly perturb the Coulombic potential. The ionization of an electron may occur not just from the valence orbital, but also from a core orbital, if the photon energy is high enough to energetically access electrons in the core orbital. This leads to inner-shell ionization, and is described in detail in the next section.

4.3 Inner-Shell Ionization

In inner-shell ionization, an electron is ionized from a core atomic orbital to generate a core hole. The inner-shell vacancy is filled by a fast Auger decay or cascade which is accompanied by the ejection of at least one more electron to generate a multiply charged ion [86–88]. To remove a core electron from a specific site in the molecule, the photon energy must exceed the binding energy of the core electron, and the atomic absorption cross-sections for photoionization (σ_{abs}) must favour a specific site in the molecule [77, 81–83]. Methyl iodide (CH_3I) is used as an example in the following discussion to highlight the importance of these two criteria. At a photon energy of

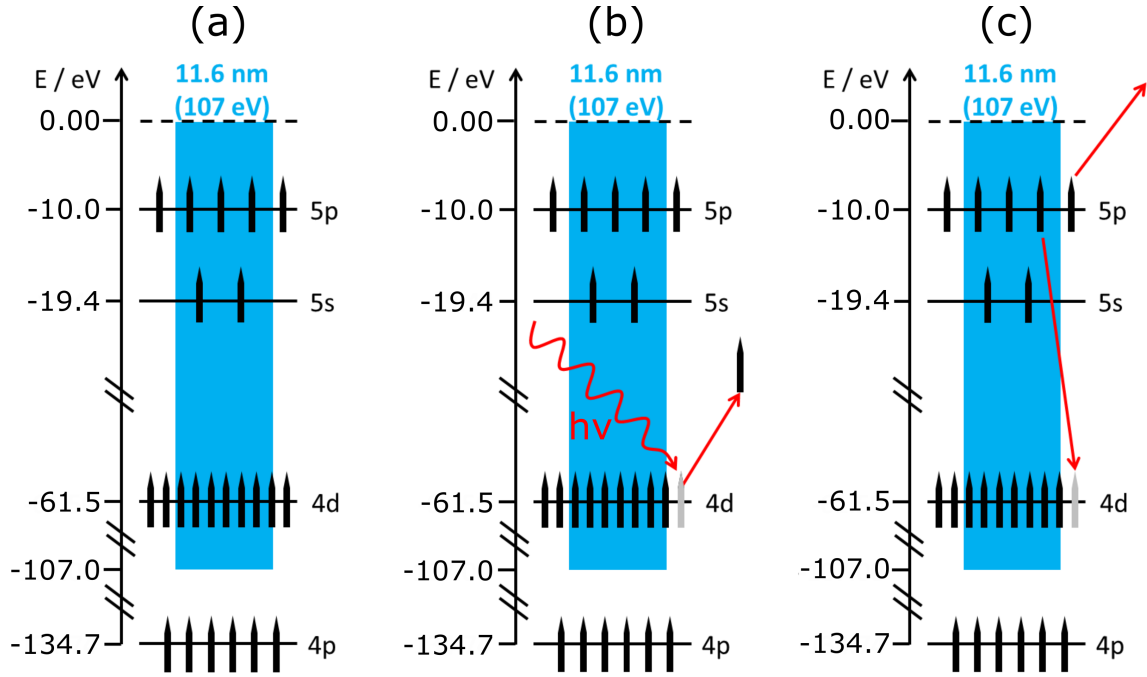


Figure 4.2: The energy scheme of the four highest occupied atomic orbitals of atomic iodine. The binding energies of atomic iodine are shown from Reference [240]. Panel (a) presents the orbitals that are energetically accessible at 107 eV shown by the blue shading. Panel (b) shows the creation of a core-hole after the ejection of an electron from the 4d atomic orbital following the absorption of a 107 eV photon [77, 81–83]. Panels (c) illustrates the typical Auger decay [86, 88, 241] mechanism that occurs following the ejection of an electron from the 4d atomic orbital. See text for details.

107 eV, the iodine atom has a σ_{abs} value that is at least seven times greater than that of any other atom in CH_3I (see Table 4.1). Thus, the absorption of an XUV photon is initially strongly localized on the iodine atom in the molecule [77, 81–83]. For the sake of simplicity, the inner-shell ionization of atomic iodine is discussed, as shown in Figure 4.2. Although three atomic orbital shells (5p, 5s and 4d) in atomic iodine are energetically accessible at 107 eV, as shown in Figure 4.2(a), ionization mainly occurs from the 4d orbital since the absorption cross-section of the 4d orbital is ~ 25 times greater than the 5p or 5s atomic orbitals (see Table 4.2). Therefore, the absorption of a 107 eV photon by CH_3I leads to the inner-shell ionization of the 4d orbital of iodine,

	Iodine	Carbon	Hydrogen	Fluorine	Chlorine	Neon
σ_{tot} (Mb)	3.56	0.47	0.02	2.38	0.97	3.47

Table 4.1: Calculated total atomic absorption cross-section, σ_{tot} , for photoionization at the photon energy of 107 eV based on References [240, 242, 243]. The SI unit for Mb is 10^{-18} m^2 .

	I(4d)	I(5s)	I(5p)	C(2s)	C(2p)	H(1s)	F(2p)	F(2s)
σ_{abs} (Mb)	3.21	0.12	0.13	0.33	0.14	0.02	1.85	0.53

Table 4.2: Calculated atomic cross-sections for photoionization at the photon energy of 107 eV based on References [240, 242, 243]. The SI unit for Mb is 10^{-18} m^2 .

and generates a localized core-hole on the iodine atom that is in a highly excited state [77, 81–83], as shown in Figure 4.2(b). Many relaxation pathways exist that can dissipate energy and fill the core-vacancy, as discussed further in the following section.

4.4 Relaxation Processes

The dissipation of energy and filling of core vacancies can occur through radiative or non-radiative relaxation processes. Fluorescence decay is a typical radiative relaxation process which sees the core hole filled by a higher lying electron, leading to the emission of a photon [241, 244, 245]. The emitted photon has an energy, $E_{h\nu}$, that is characteristic of the energy difference between the initial, E_i , and final, E_f , energies of the atomic orbitals that the electron occupied before and after filling the core hole, respectively,

$$E_{h\nu} = E_f - E_i. \quad (4.3)$$

Since only a photon (and not an electron) has been emitted from the particle in fluorescence decay, the charge state of the particle remains the same.

Auger decay is a non-radiative relaxation process that leads to the ejection of a second electron with a specific kinetic energy [86, 88, 241]. In the example of CH_3I at 107 eV, an Auger decay triggers the movement of an electron from the higher-lying valence orbital to fill the core-vacancy in the 4d orbital, as shown in Figure 4.2(c). The excess energy is carried away by a second electron, referred to as the Auger electron [86, 88, 241], as shown in panel (c). This ultimately leaves two holes in the valence shell, with the charge on the ion increasing by one to generate a dication. Depending on the electronic states involved in the first Auger decay, the molecular dication can,

in some cases, be in an excited state that could then decay by a second Auger process in a so-called Auger cascade. Alternatively, the first Auger process may also result in the simultaneous emission of two Auger electrons in a so-called double Auger process [87, 88, 241, 245]. Both of these pathways can generate a trication. As mentioned earlier, inner-shell ionization requires a laser pulse of sufficiently high photon energy, with experimental sources discussed in the following section.

4.5 XUV and X-Ray Lightsources

In this section, an overview is given of the available XUV and X-ray lightsources that are required to access the high photon energies needed to ionize an electron from a core orbital. Although there exist many light sources that generate XUV and X-ray light, the three most commonly used modern light sources are: synchrotrons, high-harmonic generators (HHG) or free-electron lasers (FELs).

4.5.1 High-Harmonic Generation

In HHG, a non-resonant intense laser pulse illuminates a target to eject an electron that can then recombine with the target molecule [35, 246]. As the electron recollides in strong laser fields, the sample emits high harmonics (integer multiples) of the generation beam [246] with relatively large photon energies [247, 248]. A specific harmonic can be selected through various techniques, including metallic filters [249], XUV dielectric multilayers [250], and a XUV time-delay-compensated monochromators [251]. The former two techniques are not tunable as they can only select a limited range of photon energies, whilst the latter is commonly used in the field of HHG to select a particular harmonic [252, 253].

There are various factors that determine the HHG spectrum and therefore the highest photon energy achievable [36, 38, 246, 253, 254]. These include: the driving field strength, the driving field wavelength, the pulse duration, and the type of HHG medium. The former two are the most important factors as a larger field strength and longer wavelength lead to a larger distance that the free electron will travel along

the laser field, leading to a larger kinetic energy that the electron will gain before recombination [36]. Although HHG can generate high energy photons on the order of a few femtoseconds down to the attosecond regime [34–36, 38, 39], the number of photons emitted (and the subsequent laser pulse intensity) is relatively low and decreases with increasing photon energy.

4.5.2 Synchrotron Radiation

Synchrotron facilities are accelerator-based light sources that can access photon energies of above 10 eV at a MHz repetition rate [255, 256]. Although they generate higher photon intensities than in HHG, the number of photons emitted is still not enough to access the multi-photon regime [255, 256]. Synchrotrons also generate radiation with relatively long pulse durations (50–100 ps) which cannot be used to investigate pump-probe dynamical experiments on the timescale of nuclear motion (<100 fs [49, 50]). A slicing technique can be used to generate 100 fs synchrotron pulses but with significantly lower intensity since at most 0.1% of the electron bunch can be separated [82, 257].

4.5.3 Free-Electron Lasers

Free-electron lasers [258–262] are also accelerator-based light sources, and can generate both intense ($10^{12} - 10^{14}$ photons per pulse) and ultrashort (2–300 fs) XUV and X-ray photon pulses at repetition rates of up to 27 kHz [256]. Thus, FELs provide access to the multi-photon regime at relatively high photon energies, which are currently not possible with synchrotron or HHG sources.

FELs and synchrotrons that use superconducting accelerator technology, such as the FLASH FEL, share several common principles, as illustrated in Figure 4.3. In both, a picosecond laser irradiates a photocathode to generate a very short and intense electron beam that was accelerated to relativistic energies using a superconducting linear accelerator [258, 260]. The electron beam is injected into a long, periodic arrangement of dipole magnets with alternating polarity, called an undulator, that force the trajectory of the electrons to oscillate, leading to the spontaneous emission of radiation. At

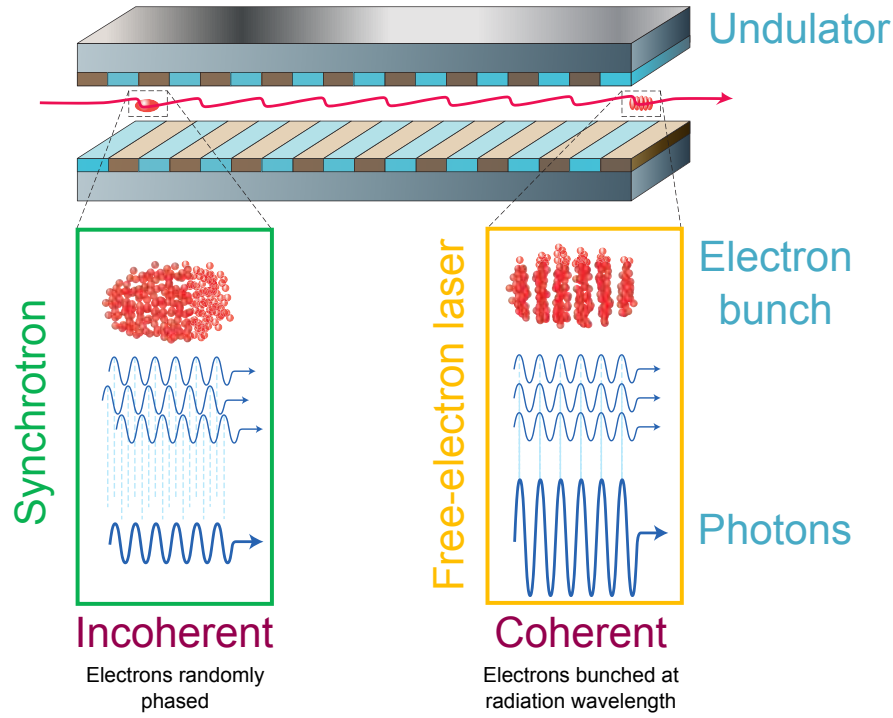


Figure 4.3: The working principle of a FEL based on superconducting accelerator technology is illustrated here. See text for detailed description. This figure was adapted from Ref. [260].

the beginning of the undulator, the radiation emitted is mostly incoherent since the electron beam that entered the undulator had initially random phase [260], as shown in Figure 4.3 (left). As the electrons travel through the undulator, they interact with their own emitted radiation to generate small coherent fluctuations in the radiation field which has the effect of bunching the electrons together, with a separation that approaches the wavelength of the emitted radiation. This is referred to as “microbunching” [260] and is unique to a FEL. At the end of the undulator, each bunch of electrons is separated by a distance equal to the wavelength of the emitted radiation, as shown in Figure 4.3 (right). Thus, an intense, femtosecond light pulse is generated through self-amplified spontaneous emission (SASE) [258] with a tunable wavelength. Several FEL facilities currently exist worldwide that can access the XUV and X-ray range with wavelengths below 0.1 nm (12.4 keV) as detailed in Table 1 of Reference [260]. Due to the spontaneous emission of free-electron lasers, significant shot-to-shot variation in the pulse energy, arrival time, x - and y -pointing direction and mean photon energy of the FEL exist. Thus, FELs are inherently relatively unstable light sources, particularly when compared to table-top optical lasers.

4.6 Laser-Induced Alignment

Laser-induced alignment of molecules provides control over the degree of spatial localization. In the presence of a non-resonant laser field, a molecule can be described by

$$\hat{H}(t) = \hat{H}_0 + \hat{V}_{\text{ind}}(t), \quad (4.4)$$

where $\hat{H}(t)$ is the total Hamiltonian at time t , $\hat{H}_0$ is the Hamiltonian under field free conditions, and $\hat{V}_{\text{ind}}(t)$ is the time-dependent induced potential experienced by a molecule in the presence of a laser field described by [54, 55, 145]

$$\hat{V}_{\text{ind}}(t) = - \sum_i \mu_i |\mathbf{E}_i(t)| - \frac{1}{2} \sum_i \alpha_{ii} |\mathbf{E}_i(t)|^2 \quad (4.5)$$

where μ_i is the molecule's permanent dipole moment, α_{ii} is the polarizability tensor component in the molecular frame, and $\mathbf{E}(t)$ is the time-dependent electric field of the laser pulse given by [55, 145]

$$\mathbf{E}(t) = E_0 \boldsymbol{\epsilon} \epsilon(t) \cos(\omega t) \quad (4.6)$$

where E_0 is the field strength, $\boldsymbol{\epsilon}$ is the unit vector along the polarization axis, $\epsilon(t)$ is the pulse envelope of the laser, and ω is the frequency of the oscillating laser field [54, 55, 145].

Alignment of molecules can be divided into the adiabatic and non-adiabatic regime depending on the pulse duration of the alignment laser. In adiabatic alignment [148, 149, 152–160], the pulse duration of the alignment laser is much longer than the molecular rotational period ($\tau_{\text{al}} \gg T_{\text{rot}}$) and the field free rotational states are adiabatically transferred to pendular states when the laser field is turned on. In the absence of the laser field, the pendular states are adiabatically transferred back to the field free states leading to the re-appearance of an isotropic spatial distribution of (unaligned) molecules. The other regime of alignment is called non-adiabatic alignment [55, 154, 263, 264] and is reached when the laser pulse is much shorter in duration compared to the molecular rotation time ($\tau_{\text{al}} \ll T_{\text{rot}}$). This regime was not used for the work

presented here and is thus not discussed any further.

4.6.1 Adiabatic Alignment

In the alignment-related work presented in this thesis, the pulse duration of the alignment laser was much longer than the timescale for molecular rotation (*i.e.* $\tau_{\text{pulse}} \gg t_{\text{rot}}$, where t_{rot} in DFIB is several hundreds of picoseconds [265]) to achieve adiabatic alignment of the molecules. Because the field oscillates so quickly compared to molecular rotation, the permanent dipole term in Equation (4.5) averages out to zero [265], and Equation (4.5) is reduced to a single sum,

$$\hat{V}_{\text{ind}}(t) = -\frac{1}{4}\epsilon^2(t) \sum_i \alpha_{ii} |E_{0,i}|^2, \quad (4.7)$$

with the additional factor of 1/2 arising from the time average of $\cos(\omega t)^2$ [55, 145].

However, electrons in a molecule can still interact with the AC field of a non-resonant laser, and as a result the electrons are slightly displaced from their equilibrium position to induce a dipole moment in the molecule. This exerts a torque onto the molecules which guides them towards the lowest energy configuration. In the laboratory frame, this has the effect of forcing the most polarizable axis (MPA) of the molecule to align parallel to the polarization axis of the laser field. This is referred to as one-dimensional (1D) alignment of molecules, and can be achieved by using a linearly polarized alignment pulse.

Confinement of molecules in all three molecular axes is termed three-dimensional (3D) alignment, and is achieved by also confining the second most polarizable axis (SMPA) of the molecule. An elliptically polarized alignment pulse could be used to achieve 3D alignment of molecules since the most and second most polarizable (SMPA) axes of molecules can be confined along the major and minor components of elliptically polarized light. Examples of the spatial distributions of unaligned, 1D-aligned and 3D-aligned molecules are shown in Figure 4.4(a)-(c), respectively. The inset in the figure shows a sketch of the MPA and SMPA in 2,6-difluoriodobenzene. The MPA is parallel to the C-I axis, and the SMPA is perpendicular to the MPA and in the plane of the

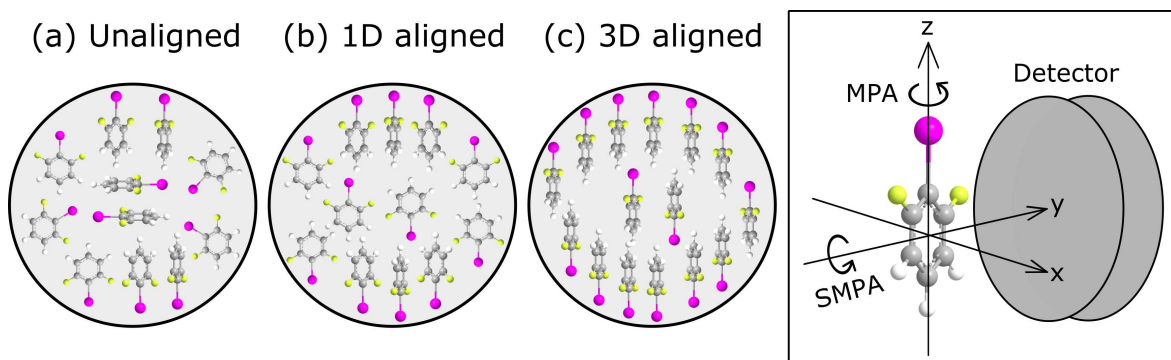


Figure 4.4: Schematic of the spatial distribution of 2,6-difluoriodobenzene molecules that are (a) unaligned, (b) 1D-aligned, and (c) 3D-aligned using a nanosecond alignment pulse. The inset shows a sketch of the most polarizable axis (MPA) and the second most polarizable axis (SMPA) in 2,6-difluoriodobenzene. The MPA is parallel to the C-I axis, while the SMPA is perpendicular to the MPA and in the plane of the molecule.

molecule.

Figure 4.5 shows the adiabatic transfer of the field free rotational states to the corresponding pendular states. The initial rotational distribution directly determines the occupation of pendular states, and the lowest lying pendular state giving the most tightly confined spatial distribution of molecules [145]. Therefore, the highest degree of

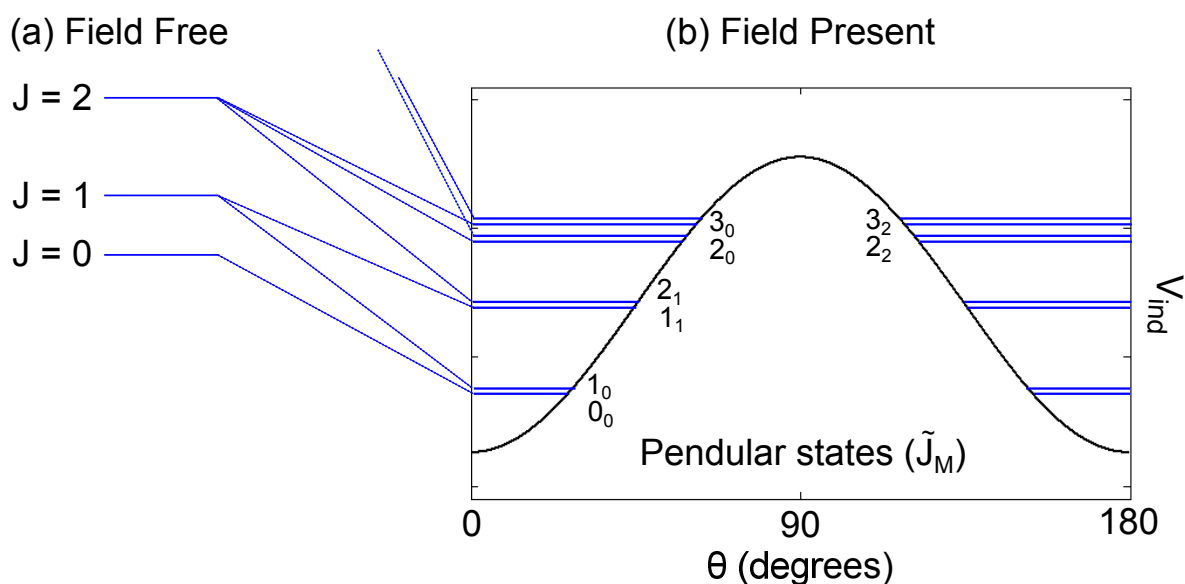


Figure 4.5: An illustration of how the (a) lowest lying rotational states (J) in the absence of a field are adiabatically transferred (broken lines) to the corresponding (b) pendular states in the presence of a long-pulse laser field. The angle between the polarization axis of the alignment pulse and the MPA of the molecule is given by θ . In the presence of the field, a nearly degenerate pair of pendular states, $\tilde{J}_M$, are formed. Here, $\tilde{J}$ is the rotational angular momentum quantum number, and M is the magnetic quantum number [145]. This figure was adapted from Reference [145].

alignment is achieved with: the coldest initial rotational distribution, the most intense laser alignment field, and the highest polarizability tensor in the molecule [55, 145].

4.6.2 Mixed-Field Orientation

In the presence of a static electric field, the nuclear framework of molecules has time to adjust to the direction of the field. As a result, molecules experience an induced potential in a static electric field [145]

$$\hat{V}_{\text{stat}}(t) = - \sum_i \mu_i |\mathbf{E}_i^{\text{stat}}(t)|, \quad (4.8)$$

where μ_i is the permanent dipole moment and $\mathbf{E}_i^{\text{stat}}(t)$ is the static field strength at time t .

If a polar molecule is exposed to a static electric field and a non-resonant laser field, the permanent dipole moment will no longer average out to zero, and the molecule will experience an induced potential as given by Equation (4.5). In the molecular frame, the lowest energy configuration occurs when the permanent dipole moment follows the direction of the static electric field to preferentially orient the molecule. In the laboratory frame, if the angle between the polarization axis of the YAG alignment pulse and the static electric field, β , is not 90° , then the up-down symmetry in molecules that is present in the alignment-only case is broken, and molecules are preferentially oriented in space. Mixed-field orientation [62, 145, 150, 151, 158, 266] is achieved experimentally by rotating the polarization axis of the YAG pulse such that it is no longer perfectly parallel to the detector plane (*i.e.* $\beta \neq 90^\circ$). Further details of orientation are presented in Section 7.3.4 of Chapter 7.

4.7 Summary

In summary, the principles of Coulomb explosion imaging have been discussed in this chapter, including details on the ionization schemes and possible relaxation processes that could generate multiply charged molecular ions in order to Coulomb explode a

molecule. Details of laser-induced alignment as well as mixed-field orientation were also given. In the following chapter, the structure of difluoroiodobenzene (DFIB) and dihydroxybromobenzene isomers are identified and compared through their Coulomb explosions induced by strong-field ionization. A sample containing a mixture of two DFIB isomers is also investigated and covariance analysis is used to identify the two structural isomers, which would not be possible through diffraction methods [267].

Chapter 5

Pure and Mixed Isomer

Identification Using Covariance

Analysis

5.1 Introduction

The geometric structure of a molecule can be identified using a variety of methods, including: X-ray diffraction [33, 259, 261, 267–273], conventional electron diffraction [274–278], laser-induced electron diffraction [36, 279–283], photoelectron imaging [82, 152, 159, 284], and Coulomb explosion imaging [54–62, 71, 79, 138–140].

In X-ray and electron diffraction, an incident beam of X-rays or electrons can collide and diffract from the atoms in a molecule towards various directions [268]. The resulting diffraction pattern recorded, with, for example, a pnCCD detector (X-ray), can be used to reconstruct the structure of the molecule. The method of X-ray crystallography, which is based on the X-ray diffraction technique, has been widely used to determine the structure of crystallised samples. Chapman *et al.* demonstrated the ability to record snapshots of single-crystals using the method of X-ray nanocrystallography [270]. However, many biologically relevant molecules, such as proteins, cannot be crystallised, and so other alternatives in obtaining structural information on these molecules must

be sought.

X-ray free-electron lasers (XFELs) [258–261, 271] provide a plethora of opportunities to study the structure of molecules in the gas, liquid and solid phases. The ultrabright, ultrafast X-ray optical pulses generated by XFELs can interact with a sample to produce diffraction patterns [259, 261]. The potential of atomically resolving non-crystallized structures by XFELs is particularly attractive given that they can be used in femtosecond-resolved pump-probe measurements to monitor the structure of a sample in ‘real-time’ [259, 261, 267, 271, 272]. In this pump-probe arrangement, a pump pulse initiates the reaction of interest, and the X-ray pulse generates X-ray diffraction patterns of the sample at a series of pump-probe delays.

Several variations of the electron diffraction technique currently exist. In conventional electron diffraction [274–276], a beam of electrons collide and diffract from the sample in a head-on ‘full’ collision. Laser-induced electron diffraction [36, 279–282] is based on the same principle as attosecond pulse generation [36, 279]: an intense laser pulse ionizes a molecule and the ejected electron is driven back by the strong laser fields to re-collide and diffract from the molecular ion. In photoelectron imaging [82, 152, 159, 284], the inner-shell ionization of a molecule ejects an electron from a core orbital at a specific site in the molecule. As the electron leaves the molecule, it can collide and diffract from the atoms in the molecule to image the molecule from ‘within’ [82, 152, 159, 284].

These diffraction-based methods have provided structural information on isolated gas-phase molecules such as laser-aligned I_2 [273], CF_3I [280], 1-ethynyl-4-fluorobenzene [152, 159] and 1,4-dibromobenzene [159]. X-ray lasers have also been used to image the structure of a single non-crystalline mimivirus particle through X-ray diffraction with a single X-ray pulse [269]. Küpper *et al.* [271, 272] demonstrated the ability to count the number of diffracted X-ray photons; to monitor and control radiation damage of molecules in the X-ray diffraction of isolated gas-phase laser-aligned 2,5-diiodobenzonitrile. Although diffraction-based methods provide structural information on isolated molecules with atomic resolution, a dense and pure sample of the molecule is required [267, 271]. The latter is particularly problematic if several isomers of the

molecule are present since each isomer has a unique diffraction pattern, and averaging over these patterns can distort structural information [267]. Significant efforts have been undertaken to overcome this problem by purifying the molecular beam sample using electrostatic deflectors to obtain one specific isomer of a molecule [266, 285–289], and by controlling the spatial orientation of molecules using laser-induced alignment [55, 148, 149, 152–160, 263, 264] and mixed-field orientation [62, 145, 150, 151, 266] in the interaction region.

An alternative to these diffraction-based methods is Coulomb explosion imaging (CEI). A range of previous studies [54–62, 71, 79, 138–140] based on CEI have shown that a rich amount of information may be obtained on the molecule’s structure, details of which were discussed in Chapters 1 and 4. Structural information can be obtained by correlating the emission direction of the recoil ions using either coincidence or covariance analysis. The coincidence method coupled with CEI has been used to obtain structural information on small molecules [51, 65, 290], and has been used to determine the absolute configuration of the chiral molecule CHBrClF [71, 79].

Structural information on larger molecules, such as 3,5-dibromo-3',5'-difluoro-4'-cyanobiphenyl, has been obtained a time-stamping device, the PImMS1 camera, coupled CEI and covariance analysis [54, 56–59, 61, 73]. Slater *et al.* [54, 56, 58] showed that a two-fold covariance analysis of the emission direction of the recoil ions, generated by the intense 30 fs 800 nm probe pulse, revealed significant structural information on the parent molecule. A three-fold covariance analysis on the same data set by Pickering *et al.* [61] revealed the ability to identify the *R*- and *S*- axial enantiomers of 3,5-dibromo-3',5'-difluoro-4'-cyanobiphenyl due to the torsional barrier. This last example is particularly important in distinguishing CEI from diffraction-based techniques; even though two enantiomers were present in the sample, it is still possible, through CEI and three-fold covariance analysis, to distinguish and identify the two chiral structures in the PImMS data set.

This was extended to time-resolved studies of torsional motion in the same molecule by Christensen *et al.* [57], using two intense, femtosecond nonresonant “kick” pulses followed by strong-field ionization with an intense 800 nm pulse. The authors monitored

the torsional motion in the molecule by tracking the recoil angle between F^+ and Br^+ ions, which is equivalent to the angle between the plane of the two benzene rings, the dihedral angle. The authors demonstrated that a strong enhancement in torsional motion can be induced by carefully controlling the arrival-time of the second ‘kick’ pulse to coincide with the time at which the two rings are rotating towards each other [57].

In this chapter, the multi-mass imaging capability of the PImMS2 camera is used to identify and distinguish between structural isomers of difluoriodobenzene (DFIB) and dihydroxybromobenzene (DHBB) through laser-induced Coulomb explosion and two and three-fold covariance analysis of the emission direction of the recoil ions. The covariance maps from the DFIB isomers will be used to identify the isomers that are present in a DFIB mixture that contains two structural isomers in the molecular beam sample, and to estimate the ratio of the isomers in the mixture. The experimental data is compared to classical Coulomb explosion simulations. In the case of DHBB, the simulations are compared to experimental results in an attempt to identify the conformers present in the DHBB measurements as a result of the bromine-hydrogen interaction in the molecule. The impact of one-dimensional (1D) alignment of molecules in the subsequent covariance maps will also be investigated.

5.2 Experimental Methods

5.2.1 Experiment in Brief

The results presented in this chapter were generated with the Aarhus VMI spectrometer [55] at a repetition rate of 10 Hz. A brief overview of the experimental set-up and parameters is presented in this section, with a detailed description given in Chapter 2. A sample of difluoriodobenzene or dihydroxybromobenzene, which are liquids at room temperature, were placed inside the inlet compartment of the Even-Lavie valve and heated to between 100°C–120°C to generate a gaseous sample. The gaseous sample was seeded in He (total gas mixture pressure of 80 bar) and expanded through the nozzle of the pulsed Even-Lavie valve.

The resulting molecular beam was intersected by two laser pulses: a 1064 nm adiabatic alignment pulse and an 800 nm probe pulse. The 1064 nm adiabatic alignment pulse ($\tau = 10$ ns (FWHM); $I_0 = 8 \times 10^{11}$ W cm $^{-2}$) was generated with a Nd:YAG nanosecond laser at a repetition rate of 10 Hz. The 800 nm probe pulse ($\tau = 30$ fs (FWHM); $I_0 = 3.0 \times 10^{14}$ W cm $^{-2}$) was generated by a Spitfire HPR femtosecond laser system, details of which are given in Section 2.3.2.

The spectrometer was operated in crushed imaging VMI mode, and a $V_R : V_E : V_G$ voltage ratio of 1.000:0.660:0.000 was used on the ion optic assembly. An absolute voltage of 8000 V was applied to the repeller electrostatic plate. The ion imaging detector was operated with a voltage difference of around 1800 V applied across the MCPs, with a voltage difference of 3000 V was applied between the back face of the back MCP and the phosphor screen. The flashes of light emitted from the back of the P47 phosphor screen were recorded with a PImMS2 camera (~ 40 ns timing precision).

5.2.2 Covariance Analysis

The angular correlations between two or more experimental variables at relatively high count rate conditions (*i.e.* $\gg 1$ counts per shot) can be determined using covariance analysis. Covariance analysis is a statistical method which calculates the average number of times two or more variables were detected simultaneously in each acquisition cycle.

Two-Fold Covariance

As detailed in Chapter 1, the covariance between two variables, referred to as two-fold covariance, is described by [54, 56–59, 122–124]

$$Cov(X, Y) = \langle XY \rangle - \langle X \rangle \langle Y \rangle, \quad (5.1)$$

where $\langle X \rangle$ is the average number of counts measured for particle X as given by [54, 56–59, 122–124]

$$\langle X \rangle = \frac{1}{N} \sum_{i=1}^{i=N} X_i, \quad (5.2)$$

similarly for $\langle Y \rangle$, and $\langle XY \rangle$ is the average number of counts measured for particles X and Y detected in coincidence with each other [54, 56–59, 122–124]

$$\langle XY \rangle = \frac{1}{N} \sum_{i=1}^{i=N} X_i Y_i. \quad (5.3)$$

Measuring the correlations between ions at high count-rates has been successfully demonstrated with pixel-based time-stamping detectors, such as the PImMS camera, which have the capability of recording the x - and y -position of the ion as well as its arrival-time [54, 56–59]. In a typical PImMS data set, two ions of interest can be identified by choosing two ToF ranges [54]. For example, any event that falls between the time code (in bins of 40 ns) of 2304–2315 in the difluoriodobenzene (DFIB) data presented in this chapter is referred to as an I^+ ion, while any event that has a time code of between 2252–2257 is referred to as an F^+ ion. This reduces the dataset down from $324 \times 324 \times 4095$ elements to $324 \times 324 \times 18$ elements, and makes it significantly easier to calculate the covariance between two ions.

Figure 5.1 illustrates the typical steps taken in the two-fold covariance analysis to investigate correlations between the ions X and Y . Here, the two ions may have the same or different mass-to-charge ratios. In the laboratory-frame ion images, shown in panel (a), the correlations between the two ions are ‘hidden’. These correlations can be revealed by transferring from the laboratory-frame to the recoil-frame of one of the ions, and carrying out a covariance analysis on the signal fluctuations in each pixel between the two ions (step I in Figure 5.1) [54].

In this method, ion X is set as the ‘reference’ ion, and the covariance between ions X and Y in each pixel of the sensor can be calculated using [54]

$$Cov(X, Y) = \left[\frac{1}{N} \sum_{i=1}^{i=N} X_i(x_a, y_a) Y_i(x_b, y_b) \right] - \left[\frac{1}{N} \sum_{i=1}^{i=N} X_i(x_a, y_a) \right] \left[\frac{1}{N} \sum_{i=1}^{i=N} Y_i(x_b, y_b) \right],$$

where (x_a, y_a) and (x_b, y_b) are the pixel coordinates, corresponding to the positions a and b of the ions X and Y , respectively. The two ions may appear at the same or

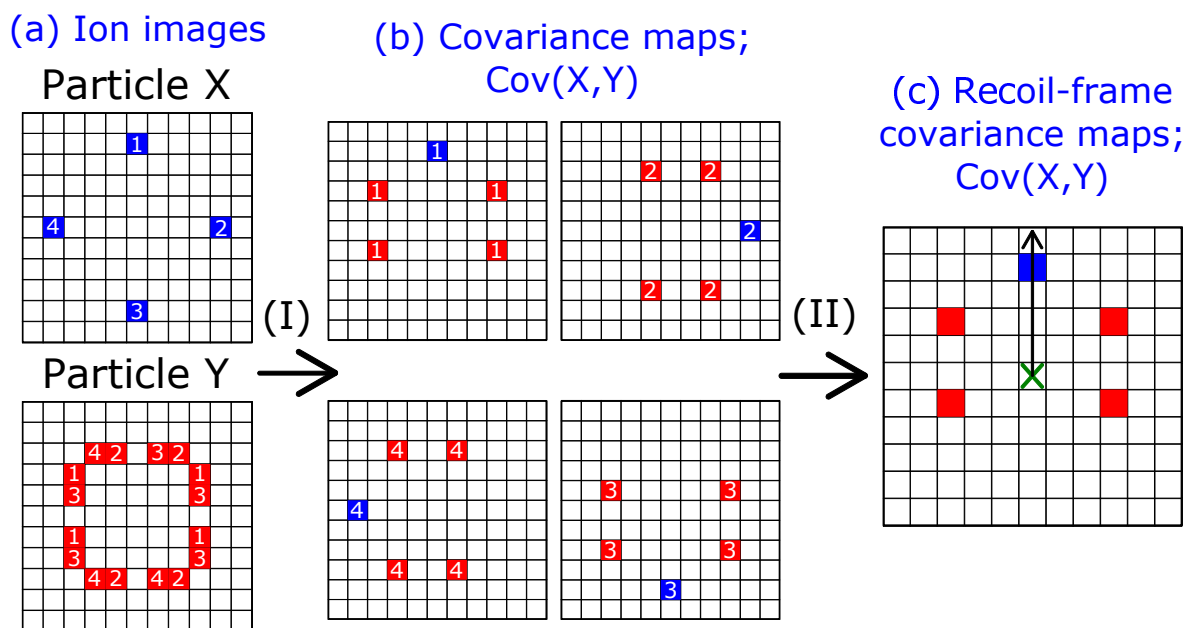


Figure 5.1: The principles of two-fold covariance analysis. Two ions, X and Y , are identified by choosing two ToF ranges, where ion X is termed the ‘reference ion’ and ion Y is the ‘plotted ion’. Their corresponding laboratory-frame ion images are shown in panel (a). Panel (b) shows the correlations between every pixel in the array of the reference ion to every pixel in the array of the plotted ion as a series of covariance maps (step I). These maps are rotated into a common recoil-frame (step II) such that the velocity vector of the reference ion lies along the vertical vector indicated by the black arrow, and ion Y is plotted relative to the reference ion, X . The numbers indicate the four molecules in which the ions originate from.

different positions on the sensor. The resulting two-fold covariance maps are shown in Figure 5.1(b), where the plotted ion, Y , is shown relative to the reference ion, X .

The covariance maps at each pixel are then rotated such that the reference ion (X) lies along a common vector (step II) to generate a ‘common recoil-frame’ covariance map, shown in panel (c). This is done by calculating the angle and radius for the plotted ion (Y) relative to the reference ion (X). The relative polar coordinates are then converted to cartesian coordinates, and the covariance value is placed at the relevant pixel coordinate on a new map (the ‘common recoil-frame’ covariance map). Here, the angle of 0° is along the vertical vector, indicated by the black arrow in panel (c), and angles between 0 - 360° are given by the clockwise rotation of the black arrow. A radius of 0 is defined by the centre of the map (green cross). This process is then repeated for every pixel in the array of the reference ion with every pixel in the array of the plotted ion.

Three-Fold Covariance

The covariance between three variables, referred to as three-fold covariance [61, 73, 122]

$$Cov(X, Y, Z) = \langle XYZ \rangle - \langle X \rangle \langle YZ \rangle - \langle Y \rangle \langle XZ \rangle - \langle Z \rangle \langle XY \rangle + 2 \langle X \rangle \langle Y \rangle \langle Z \rangle, \quad (5.4)$$

where $\langle XYZ \rangle$ is the average number of counts measured for particles X, Y and Z in coincidence with each other as described by [61, 73, 122]

$$\langle XYZ \rangle = \frac{1}{N} \sum_{i=1}^{i=N} X_i Y_i Z_i. \quad (5.5)$$

The principles of three-fold covariance analysis are illustrated in Figure 5.2. As in the two-fold case, the laboratory-frame ion images for ions X , Y , and Z , shown in panel (a), cannot directly distinguish the structure of the parent molecule. In the recoil-frame covariance map for three ions, ion X is set as the ‘reference’ ion, ion Y is designated as the ‘constrained’ ion, and ion Z is then plotted in the recoil-frame of the reference ion. The velocities of ion X are rotated to lie along a common vector, as indicated by the vertical black arrow shown in Figure 5.2. While the velocities of ion Y are constrained to a specific area of the covariance map. In the case where the velocity vector of ion Y is not constrained, as shown in panel (b), the resulting recoil-frame covariance map contains a four-fold feature which suggests that one or more plotted ions Z is located ortho and meta to the reference ion X . This four-fold feature could correspond to the presence of two enantiomers. To investigate this, the velocities of the constrained ion can be restricted to a specific area (red square, step II) which could reveal the R - or S -enantiomer of the molecule when placing the constrained area either on the top-left or top-right hand side, respectively, as shown in panel (c).

Covariance maps may have positive or negative intensity values [122]; a positive $Cov(X, Y)$ value is generated if the two fragments are detected correlated more often than uncorrelated, while the converse leads to negative $Cov(X, Y)$ values. The intensity values in the covariance maps are strongly influenced by the detection efficiency of the

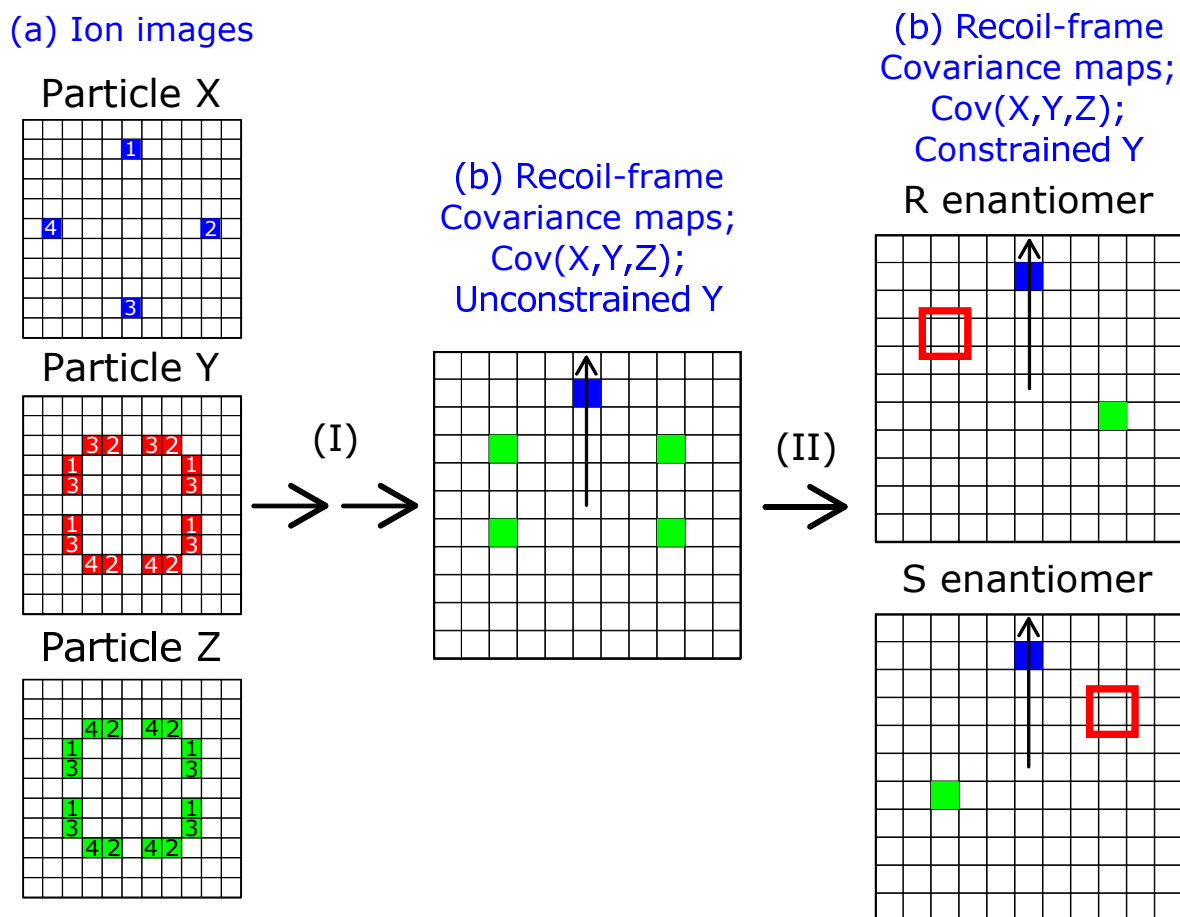


Figure 5.2: The principles of three-fold covariance analysis. Three ions, X , Y and Z , are identified by choosing three ToF ranges. Ion X is referred to as the ‘reference ion’, ion Y is the ‘constrained ion’, and ion Z is the ‘plotted ion’. Their corresponding laboratory-frame ion images shown in panel (a). In panel (b), the recoil-frame covariance map shows the correlations between every pixel in the array of the reference ion to every pixel in the arrays of the constrained and plotted ions (step I). In this map, the velocity vector of ion X is restricted to the vertical vector indicated by the black arrow, while no restrictions were applied to the velocity vector of the constrained ion, and ion Z is plotted relative to the reference ion, X . Panel (c) shows the resulting covariance map where the velocity vector of the constrained ion is restricted to a constrained area (red square, step II), with the plotted ion appearing on the opposite side as to the constrained area. Thus, the R - and S -enantiomers of the molecule can be identified by placing the constrained area to either the left or right-hand side of the arrow, respectively. The numbers indicate the four molecules in which the ions originate from.

ion detector in detecting two or more correlated ions. A handle on the detection efficiency is provided by the voltages that are applied to the ion detector, which is investigated in the following section.

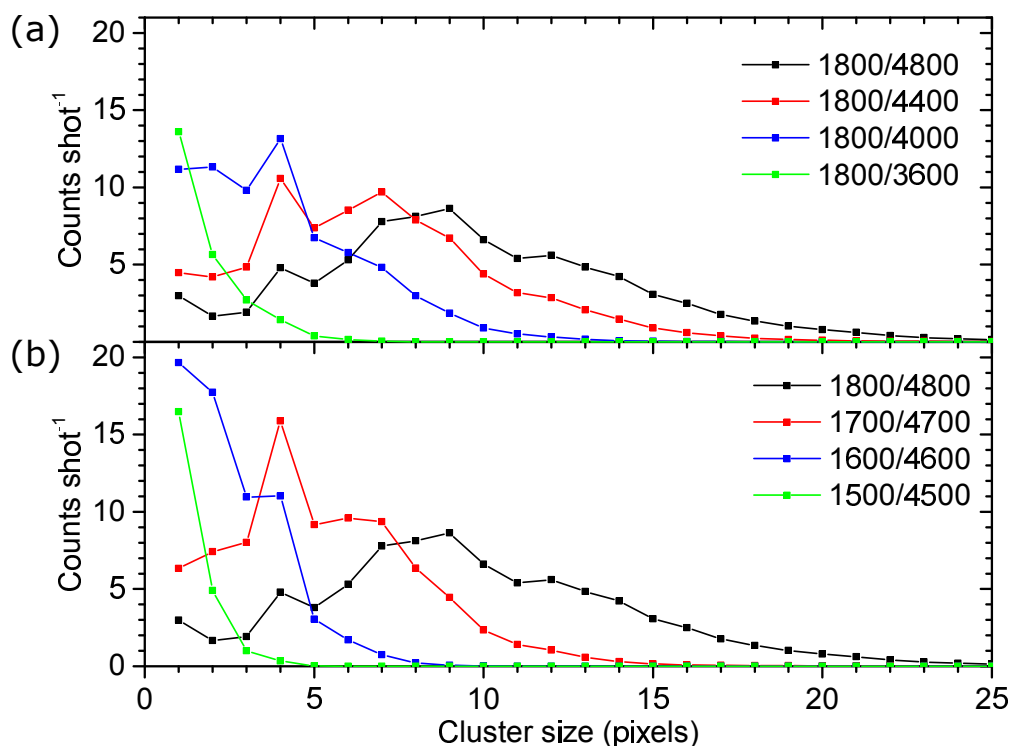


Figure 5.3: The frequency of cluster size recorded by the PImMS2 camera for various MCP/phosphor screen detector settings where (a) only the phosphor screen voltage or (b) both the MCPs and phosphor screen voltages were varied. The legend “A/B” in the figure refers to the voltage across the MCPs (A) and the voltage on the phosphor screen (B) in volts. Each ToF distribution is normalised to its corresponding total number of laser shots.

5.2.3 Optimization of Covariances

In this section, the influence of the detection efficiency on the angular correlation between two ions of interest is investigated by varying the voltages applied to the MCPs and phosphor screen. The impact of ‘centroiding’ and ‘megacentroiding’ (see Section 2.7.1 in Chapter 2) on the angular correlation of ions will also be investigated. Figure 5.3 shows the frequency of cluster size recorded by the PImMS2 sensor at various detector voltage settings following the ionization of 1D-aligned 2,6-DFIB molecules with an intense 800 nm pulse. In the top panel, the phosphor screen voltage was varied in steps of 400 V while the MCP voltage was fixed at 1800 V. In the bottom panel, the MCP and phosphor screen voltages were both varied in steps of 100 V. Decreasing the phosphor and/or MCP voltages leads to dimmer flashes of light on the phosphor screen that impact on correspondingly fewer pixels on the PImMS2 sensor. This leads to a reduction in the average cluster size, which is taken as the mean of the Poisson

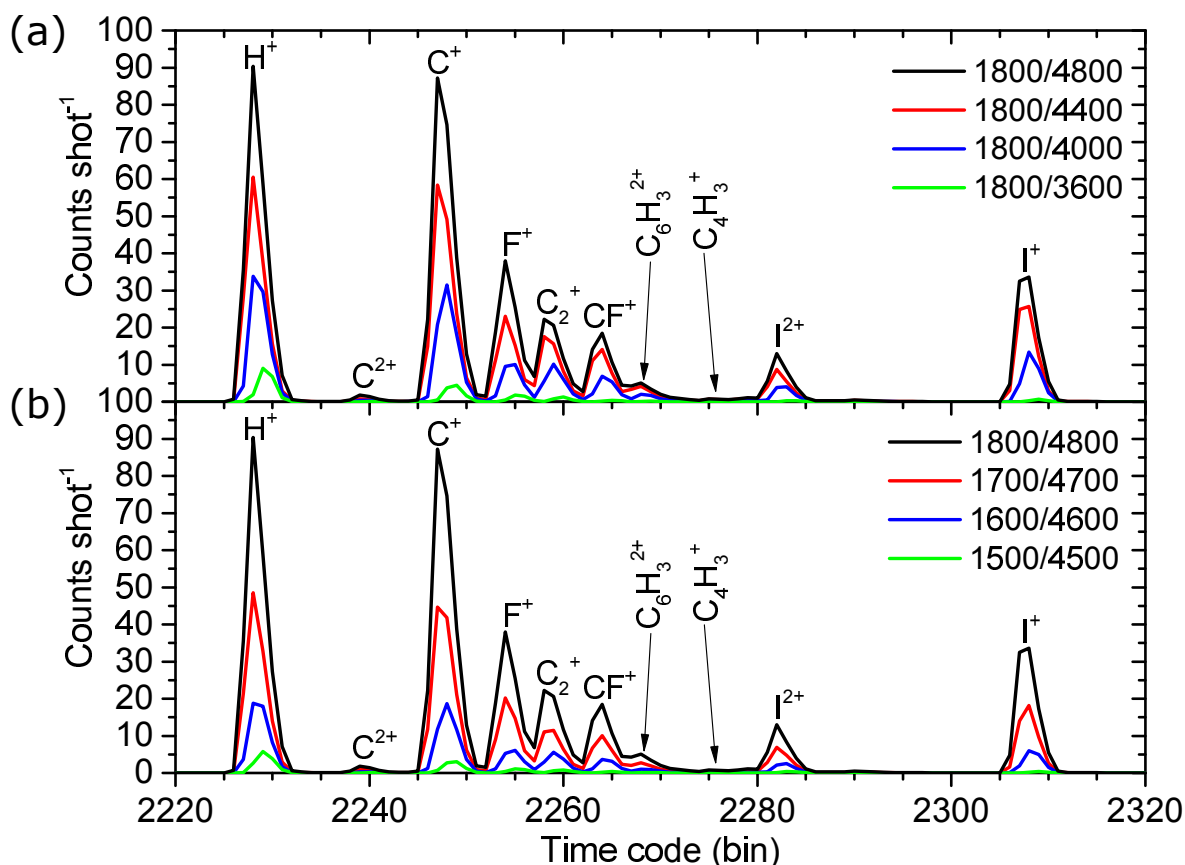


Figure 5.4: Time-of-flight spectra recorded by the PImMS2 camera for 1D-aligned 2,6-DFIB molecules following strong-field ionization with an intense 800 nm pulse polarized parallel to the detector plane, where (a) only the phosphor screen voltage or (b) both the MCPs and phosphor screen voltages were varied. The top panel corresponds variation of the the phosphor screen voltage, while the bottom panel corresponds to the variation of both phosphor screen and MCP voltages. The four traces in each panel correspond to a set of MCP and phosphor screen voltage settings. The legend “A/B” in the figure refers to the voltage across the MCPs (A) and the voltage on the phosphor screen (B) in volts. Each ToF distribution is normalised to its corresponding total number of laser shots.

distributions shown in Figure 5.3.

Figure 5.4 shows the ToF traces recorded by the PImMS2 camera at various detector voltages. A decrease in the phosphor screen voltage leads to a reduction in the intensity of the ToF profile (top panel). In the bottom panel, both the MCP and phosphor screen voltages were reduced, which also lead to a reduced ToF profile intensity. Both trends are due to the reduced sensitivity and hence detection efficiency of the MCP/phosphor screen detector upon reducing their voltages.

Very few ion counts were recorded at the lowest MCP voltage of 1500 V even though the phosphor screen voltage was still relatively high (4500 V). This is unsurprising

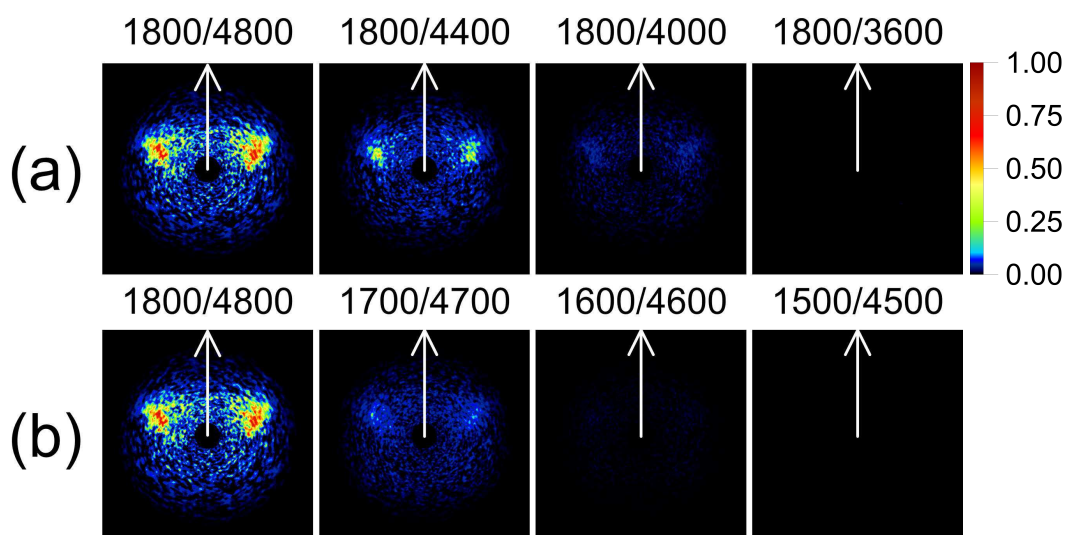


Figure 5.5: The two-fold covariance map, $Cov(I^+, F^+)$, recorded at various MCP/phosphor screen settings following the Coulomb explosion of 1D-aligned 2,6-DFIB molecules using an intense 800 nm pulse polarized parallel to the detector plane, where (a) only the phosphor screen voltage or (b) both the MCPs and phosphor screen voltages were varied. Here, I^+ and F^+ are the reference and plotted ions, respectively. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map. The label “A/B” above each row of maps refers to the voltage on the MCPs (A) and the voltage on the phosphor screen (B) in volts. Each map is generated from 16,000 laser shots worth of data and is normalized to the “1800/4800” map.

since the MCPs provide the amplification of the ion signal, while the phosphor screen converts the impact of the electrons, which originate from the back of the MCPs, into flashes of light. Therefore, if there are not many electrons hitting the phosphor then there is not much signal to detect, even if the largest voltage is applied on the phosphor screen.

The influence of the detector voltage settings on the correlation between I^+ and F^+ ions is shown in Figure 5.5 through the two-fold covariance map, $Cov(I^+, F^+)$, where I^+ is the reference ion, and F^+ is the plotted ion. In panel (a), a weaker correlation between I^+ and F^+ ions was observed upon reducing the phosphor screen voltage in steps of 400 V, which is unsurprising since the flashes of light emitted are dimmer. While in panel (b), both the phosphor screen and MCP voltages were reduced in steps of 100 V. In this panel, the correlation between the two ions of interest were not detected after reducing the MCP voltage by only 200 V. Since the probability of detecting two correlated ions goes by the square of the detection efficiency, the detection of two ions

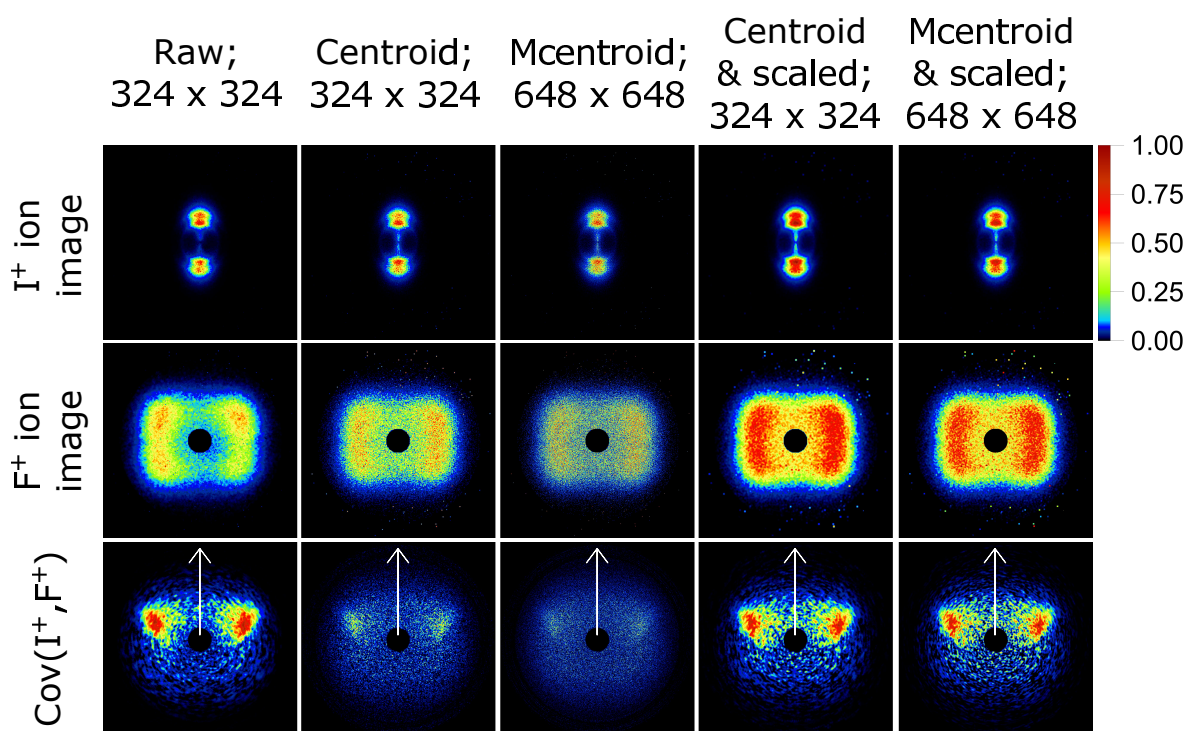


Figure 5.6: The I^+ (top row) and F^+ (middle row) ion images from the Coulomb explosion of 1D-aligned 2,6-difluoriodobenzene molecules using an 800 nm pulse polarized parallel to the detector plane. The bottom row shows covariance maps of F^+ with respect to I^+ , where I^+ is the reference ion and F^+ is the plotted ion in the map. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each covariance map. The first two columns show the raw, centroided and megacentroided data. The last two columns correspond to the scaling of each event in the centroided/megacentroided data to 3×3 and 5×5 pixel clusters. Each map is generated from approximately 50,000 laser shots.

is therefore much harder than the detection of a single ion. Thus, the covariance maps provide a strict test on the influence of the detector voltages on the detection efficiency.

Next, the impact of centroiding and megacentroiding on the ion images and the two-fold covariance maps, $Cov(I^+, F^+)$, are investigated. Figure 5.6 shows the outcome of the centroiding and megacentroiding process. The first two rows show the I^+ and F^+ ion images, while the last row shows the $Cov(I^+, F^+)$ covariance map where I^+ is the reference ion (white arrow) and F^+ is the plotted ion. The first two columns correspond to the raw and centroided data. Although the features in the ion images are better resolved in the centroided data, the overall signal level is reduced, particularly in the F^+ ion image, since the centroiding algorithm used here centroids a pixel of clusters to a single pixel. The reduction in signal level (and therefore statistics) in the centroided data leads to reduced signal:noise ratio in the $Cov(I^+, F^+)$ covariance map

when compared to the corresponding raw covariance map. In the megacentroided data, ion events are plotted in a “virtual grid” that is twice the dimension of the PImMS2 sensor. This leads to a further reduction in signal:noise in the ion images even though the features are better resolved than in the centroided and raw data. The signal:noise is significantly reduced in the megacentroided covariance map and the correlations between I^+ and F^+ are barely observable.

To confirm that statistics were the primary reason that lead to the reduced signal:noise in the covariance maps, each event in the centroided and megacentroided data, which consists of a single pixel, were scaled to 3×3 and 5×5 pixel clusters, respectively, since the average cluster size in the raw data was 9 pixels. The resulting scaled ion images and two-fold covariance maps are shown in the last two columns of Figure 5.6. The scaled centroided/megacentroided data have similarly resolved features in the covariance map relative to the raw map, but the former contain more noise around 0° (*i.e.* near the white arrow) than the raw data. The appearance of noise in a covariance map is referred to as ‘falsely correlated’ signal or ‘false’ coincidences. As a result, the corresponding PImMS2 data that is presented in the remainder of this chapter was not centroided/megacentroided, and instead the raw data was used which yielded excellent ion images as well as the highest quality two- and three-fold covariance maps.

In the rest of this chapter, experimental results are presented to investigate the scope of the CEI technique to give structural information on several structural isomers of difluoriodobenzene (DFIB) and dihydroxybromobenzene (DHBB). A mixture measurement that contains two structural isomers of DFIB in the molecular beam sample is also investigated to test the limits of this technique, in particular in its ability to identify the structural isomers present in the mixture. Simulated results are also presented, which act as a rough comparison to the experimental data. In the case of DHBB, the simulated results are compared to the experimental data to try to identify the conformers that are present in the experimental data.

5.3 Identification of DFIB Isomers

In this section, the ToF spectra, ion images and subsequent two- and three-fold covariance maps are used to identify the structural isomers of difluoroiodobenzene (DFIB) in four separate measurements that each contain a particular pure isomer of DFIB: 3,5-DFIB, 2,6-DFIB, 2,5-DFIB, and 2,4-DFIB. Each molecule was multiply ionized with an intense 800 nm 40 fs pulse, leading to the Coulomb explosion of the molecule. The resulting fragment ions were recorded with the PImMS2 camera.

5.3.1 ToF Spectra and Ion Images

The ToF spectra of the four pure isomers of DFIB recorded by the PImMS2 camera are shown in Figure 5.7 following strong-field ionization by an intense 800 nm pulse: 3,5-DFIB (red trace), 2,6-DFIB (black trace), 2,4-DFIB (green trace) and 2,5-DFIB (blue trace) pure isomers. In the same figure, the ToF trace for a mixture of 1D-aligned 3,5-DFIB and 2,4-DFIB molecules is also shown (yellow trace).

The corresponding ion images for the most significant ion fragments (H^+ , F^+ , I^{2+} , and I^+) are shown above the ToF spectrum (grey shaded peaks). These corresponding ion images show several distinct differences, particularly for H^+ and F^+ ions. For I^+ and I^{2+} , two highly localized maxima exist in their respective ion images which indicate the polarization axis of the Nd:YAG alignment laser. This is a consequence of the C-I axis, the most polarisable axis (MPA) in the molecules, aligning parallel to the polarization axis of the adiabatic alignment laser and the iodine ions being ejected along that axis. A degree of alignment of up to $\langle \cos^2 \theta_{2D} \rangle = 0.95$ was extracted from the I^+ ion images in these measurements.

The F^+ ions, in for example 2,4-DFIB, are ejected either along the MPA or as two torus-shaped distributions around the alignment axis. In the same molecule, the H^+ ion image contains a four-fold feature, which corresponds to the presence of hydrogens in positions ortho and meta to the iodine in the molecule. The ion images for 3,5-DFIB and 2,5-DFIB are very similar and it is almost impossible to distinguish these two structural DFIB isomers from each other.

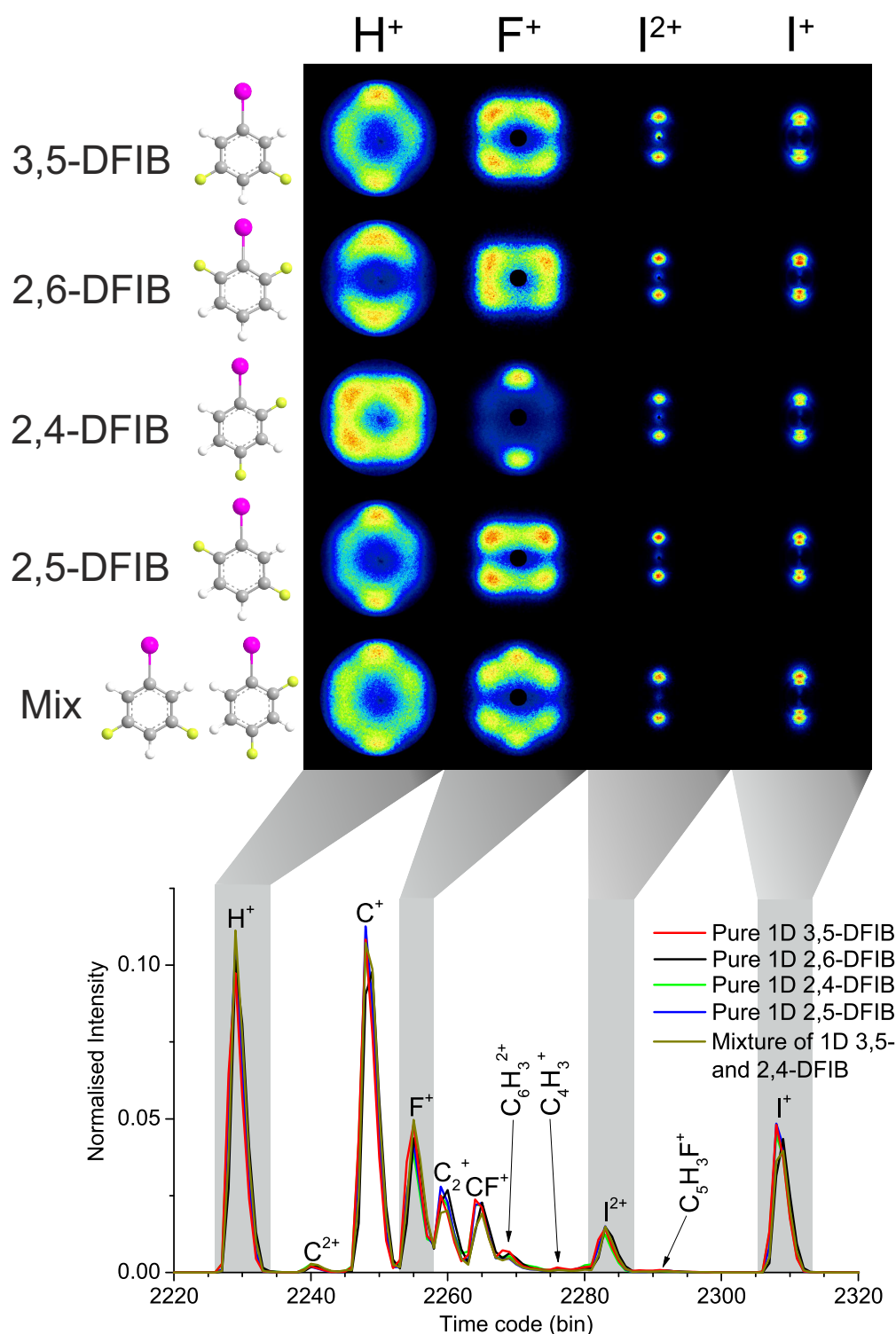


Figure 5.7: Time-of-flight spectra recorded by the PImMS2 camera for 1D-aligned DFIB molecules following strong-field ionization with an intense 800 nm pulse polarized parallel to the detector plane. Measurements for 3,5- (red trace), 2,6- (black trace), 2,4- (green trace), and 2,5- (blue trace) pure isomers of DFIB are shown along with a mixture of 3,5- and 2,4-DFIB isomers (yellow trace). The corresponding laboratory-frame ion images are shown above the assigned time-of-flight peaks for the most significant ion fragments (H^+ , F^+ , I^{2+} , and I^+). The grey shading indicates the time-of-flight range used to generate each ion image. Each ToF distribution is normalised to its corresponding total ion count.

In the measurement of the mixed isomers, it is very difficult to identify the structural isomers that are present in the mixture just from their ion images. In the following section, the angular correlations between the momentum of two ions are plotted using the covariance method, which generate distinct and unique covariance maps for each pure structural isomer of DFIB, which can be used to interpret the covariance maps for the mixed measurement.

The two-fold covariance maps for 1D-aligned DFIB molecules are shown in Figures A.1 - A.4 in Appendix A, corresponding to 3,5-DFIB, 2,6-DFIB, 2,4-DFIB, and 2,5-DFIB pure isomers. The covariance maps reveal significant structural information that was hidden in the ion images shown in Figure 5.7. All four sets of covariance data are unique, and can therefore be used to identify each of the four isomers in the pure measurements.

5.3.2 Identification of Structural Isomers

In this section, the most significant two-fold covariance maps are shown, in Figure 5.8, for four isomers of DFIB. The experimental and pBasex reconstructed data from this Figure will be used in the following discussion to identify the structure of each DFIB isomer present in the four measurements. Each column in the figure corresponds to the following two-fold covariance maps: $Cov(I^+, F^+)$, $Cov(I^+, H^+)$, $Cov(F^+, H^+)$, $Cov(F^+, F^+)$, and $Cov(H^+, H^+)$.

The first row of images in each panel correspond to the experimental maps. The second row of images show a slice out of the reconstructed 3D momentum distribution of ions that is generated from the pBasex-inversion of the corresponding experimental map [213]. The features in the pBasex slice images are better resolved than in the corresponding raw experimental crushed images. Although this section focusses mainly on the experimental results, the corresponding simulated data for the first two rows of images are also shown in the final two rows of Figure 5.8. A brief discussion of the simulated data will be given later in Section 5.3.4.

Figure 5.9 shows the angular distributions extracted from the maps in Figure 5.8. The angular distributions of the pBasex data are clearly better resolved than the cor-

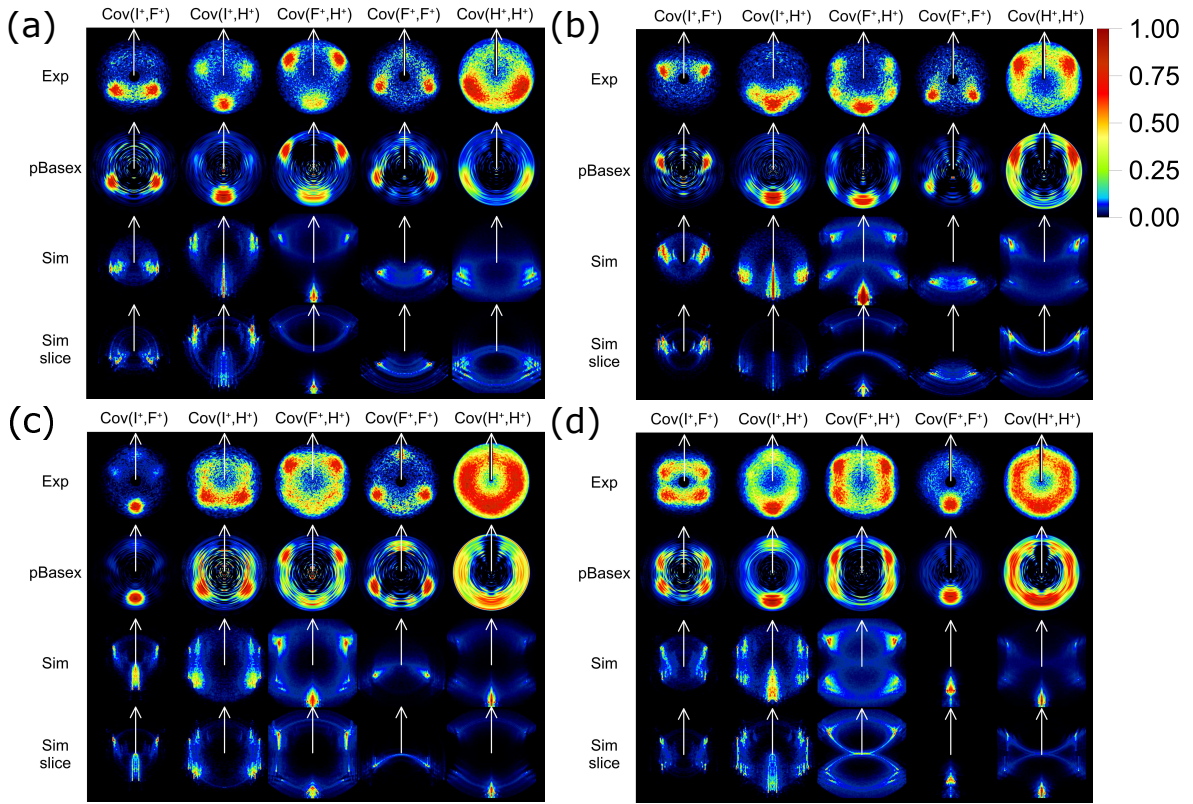


Figure 5.8: Selected two-fold recoil-frame covariance maps, $Cov(X, Y)$, of 1D-aligned: (a) 3,5-DFIB, (b) 2,6-DFIB, (c) 2,4-DFIB and (d) 2,5-DFIB. The four rows correspond to the raw experimental crushed data (top row), the pBasex slice data (second row), the simulated crushed data (third row), and the simulated slice data (bottom row). Each column presents a two-fold covariance map, $Cov(X, Y)$, with the reference ion denoted as X and the plotted ion denoted as Y . The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map.

responding raw experimental data since the latter corresponds to a slice of the reconstructed Newton sphere. Therefore, the recoil angle of the plotted ion relative to the reference ion was extracted from the pBasex data by fitting a sum of Gaussians to the pBasex angular distributions. The recoil angles, taken as the mid-point of each Gaussian fit, are listed in Table 5.1.

In the $Cov(I^+, F^+)$ map in panel (a) of Figure 5.8, the F^+ ions are ejected at 122° and 238° relative to I^+ , and so the two fluorine atoms occupy the meta positions of the benzene ring relative to iodine. This agrees with the angle of 120° measured by Rolles and coworkers [291] through an electron-ion-ion coincidence experiment on the inner-shell ionization of unaligned 2,6-DFIB performed with synchrotron radiation at 107 eV (11.6 nm).

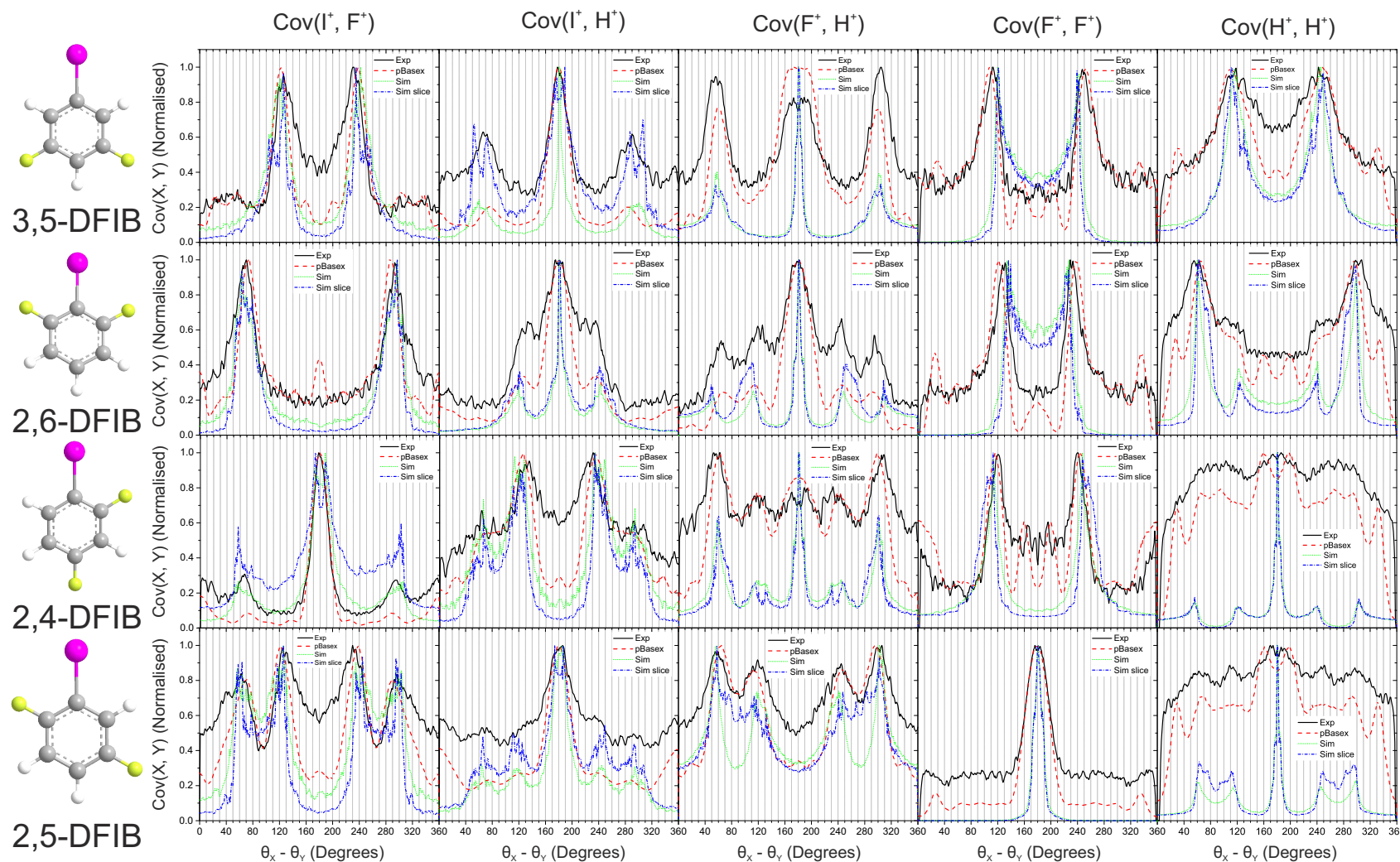


Figure 5.9: Angular distributions extracted from the two-fold covariance maps in Figure 5.8. The distributions for the raw experimental crushed data (black solid trace), pBasex slice data (red dashed trace), simulated crushed data (green dotted trace), and the simulated slice data (blue dash-dotted trace) are shown. Each distribution has been normalised to its maximum intensity.

	$Cov(I^+, F^+)$	$Cov(I^+, H^+)$	$Cov(F^+, H^+)$	$Cov(F^+, F^+)$	$Cov(H^+, H^+)$
3,5-DFIB	121.6(2)°, 238.4(2)°	77.0(2)°, 180.0(0)°, 283.0(2)°	62.0(3)°, 180.0(3)°, 298.0(3)°	105.5(5)°, 254.3(5)°	111.5(7)°, 248.2(7)
2,6-DFIB	73.6(1)°, 286.5(1)°	124.0(1)°, 180.0(0)°, 236.1(1)°	68.4(4)°, 111.6(3)°, 179.0(1)°, 246.4(3)°, 289.6(4)°	120.5(1)°, 238.5(1)°	62.3(5)°, 109.2(9)°, 251.1(9)°, 298.7(5)°
2,4-DFIB	72.1(6)°, 180.0(0)°, 287.9(6)°	76.6(8)°, 125.6(3)° 234.5(3)°, 283.5(8)°	61.9(3)°, 112.7(4)°, 180.0(4)°, 247.3(4)°, 298.1(3)°	115.4(4)°, 244.2(4)°	-
2,5-DFIB	65.8(3)°, 123.3(2)° 236.7(2)°, 294.2(3)°	73.6(2)°, 122.0(2)°, 180.0(0)°, 238.0(2)°, 286.4(2)°	63.8(3)°, 111.6(4)°, 248.4(4)°, 296.2(3)°	179.3(1)°	68.7(16)°, 105.0(23)°, 179.5(7)°, 256.0(23)°, 292.4(15)°
Mixture	54.9(2)°, 123.9(1)°, 179.4(0)°, 235.4(2)°, 305.3(2)°	75.4(2)°, 124.5(2)°, 179.5(0)°, 234.8(2)°, 285.3(1)°	69.7(1)°, 123.7(2)°, 178.7(0)°, 233.4(2)°, 290.7(1)°	108.4(18)°, 251.3(18)°	109.2(15)°, 250.7(15)°

Table 5.1: Angle of recoil extracted from the two-fold $Cov(X, Y)$ covariance maps for four isomers of DFIB. The error in the recoil angles is given by the values in the brackets and corresponds to the fitting error.

In panel (b), the F^+ ions are ejected at 74° and 287° to the I^+ ion, and so the fluorine atoms occupy the ortho positions of the molecule relative to iodine. This is slightly larger than the angle of 61° in the equilibrium geometry of the neutral 2,6-DFIB molecule [291]. Rolles and coworkers [291] measured a much larger angle of 84° , with the large discrepancy attributed to the repulsion that exists between the I^+ and F^+ ion fragments in 2,6-DFIB. The 13° discrepancy observed in the data shown in panel (b), is likely due to the same reason. Since the discrepancy in this work (13°) was not as large as in the synchrotron measurements of Rolles and coworkers (23°), it is concluded that weaker repulsion forces were present between the I^+ and F^+ fragments in this study when compared to the synchrotron measurements. This may be explained by the inner-shell case possessing a higher charged molecular ion and/or due to the charge migration from the iodine site to the rest of the molecule.

Next, the $Cov(F^+, F^+)$ maps are investigated to confirm that the features in the $Cov(I^+, F^+)$ maps correspond to a molecule containing two fluorine atoms instead of one fluorine atom. If only one fluorine atom was present in the molecule then there should not be any positive intensity signal in the $Cov(F^+, F^+)$ map. The $Cov(F^+, F^+)$ maps in both panels (a) and (b) have two localized maxima, corresponding to the ejection of F^+ ions at approximately 120° and 240° . This confirms the presence of two fluorine atoms in the molecule since the first F^+ ion is detected in coincidence with a second F^+ ion.

The $Cov(I^+, H^+)$ maps provide further clues on the identity of the isomers in panel (a) and (b). In the former panel, the hydrogen atoms occupy both the ortho and para positions in the molecule since the H^+ ions are ejected at 76° , 180° and 283° with respect to the I^+ ion. While in panel (b), the hydrogen atoms occupy the meta and para positions of the molecule since H^+ is ejected at 126° , 180° and 234° to the I^+ ion. These three covariance maps have clearly demonstrated that the data presented in panels (a) and (b) correspond to 3,5-DFIB and 2,6-DFIB, respectively.

The $Cov(I^+, F^+)$ map in Figure 5.8(c) shows that the fluorine atoms occupy both the ortho and para positions of the molecule since F^+ is ejected at 72° , 180° and 288° relative to I^+ . In this isomer, the hydrogen atoms occupy both the ortho and

para positions as can be seen by the four-fold feature in the $Cov(I^+, H^+)$ map. This suggests that only one fluorine atom occupies the ortho position of the molecule since H^+ is detected ortho to I^+ . The data presented in panel (c) therefore corresponds to 2,4-DFIB.

In panel (d), the four-fold feature in the $Cov(I^+, F^+)$ map suggests that the fluorine atoms occupy the ortho and meta positions of the molecule with respect to iodine. The F^+ ions are emitted back-to-back (*i.e.* 180°) to each other as shown by the localized feature at 180° in the $Cov(F^+, F^+)$ map. This confirms that two fluorines must exist in the molecule, one at the ortho position and the second at the meta position. It can be concluded just from these two maps that the data in panel (d) corresponds to 2,5-DFIB.

To further confirm this assignment and to investigate the origin of the four-fold feature in the $Cov(I^+, F^+)$ map of 2,5-DFIB, the three-fold covariance map $Cov(I^+, F^+, F^+)$ was calculated, details of which are given in the following section.

5.3.3 Three-Fold Covariance of 2,5-DFIB

The $Cov(I^+, F^+, F^+)$ three-fold covariance map is presented in Figure 5.10. In this map, I^+ is the reference ion, one of the two F^+ ions is restricted to the region indicated by the filled red square, and the second F^+ ion is plotted in the recoil-frame of the I^+ reference ion. In the left hand-side of panel (a), the two-fold $Cov(I^+, F^+)$ map is shown with the four features A - D marked by red squares. These four features in the $Cov(I^+, F^+)$ two-fold covariance map were used as the four constrained regions in the $Cov(I^+, F^+, F^+)$ three-fold covariance maps shown on the right hand-side of panel (a) (by the filled red squares). The $\Theta_X - \Theta_Z$ recoil angle were extracted from Gaussian fits to the angular distributions (thin red lines).

In case A, the constrained region was positioned around the top-left quadrant of the two-fold map (*i.e.* the constrained F^+ ion is positioned at the 6-position of the molecule). In the resulting three-fold covariance map, a positive signal is localized at approximately 125° relative to I^+ , as can be seen by the black trace in the angular distributions shown in Figure 5.10(b). This corresponds to the back-to-back (180°)

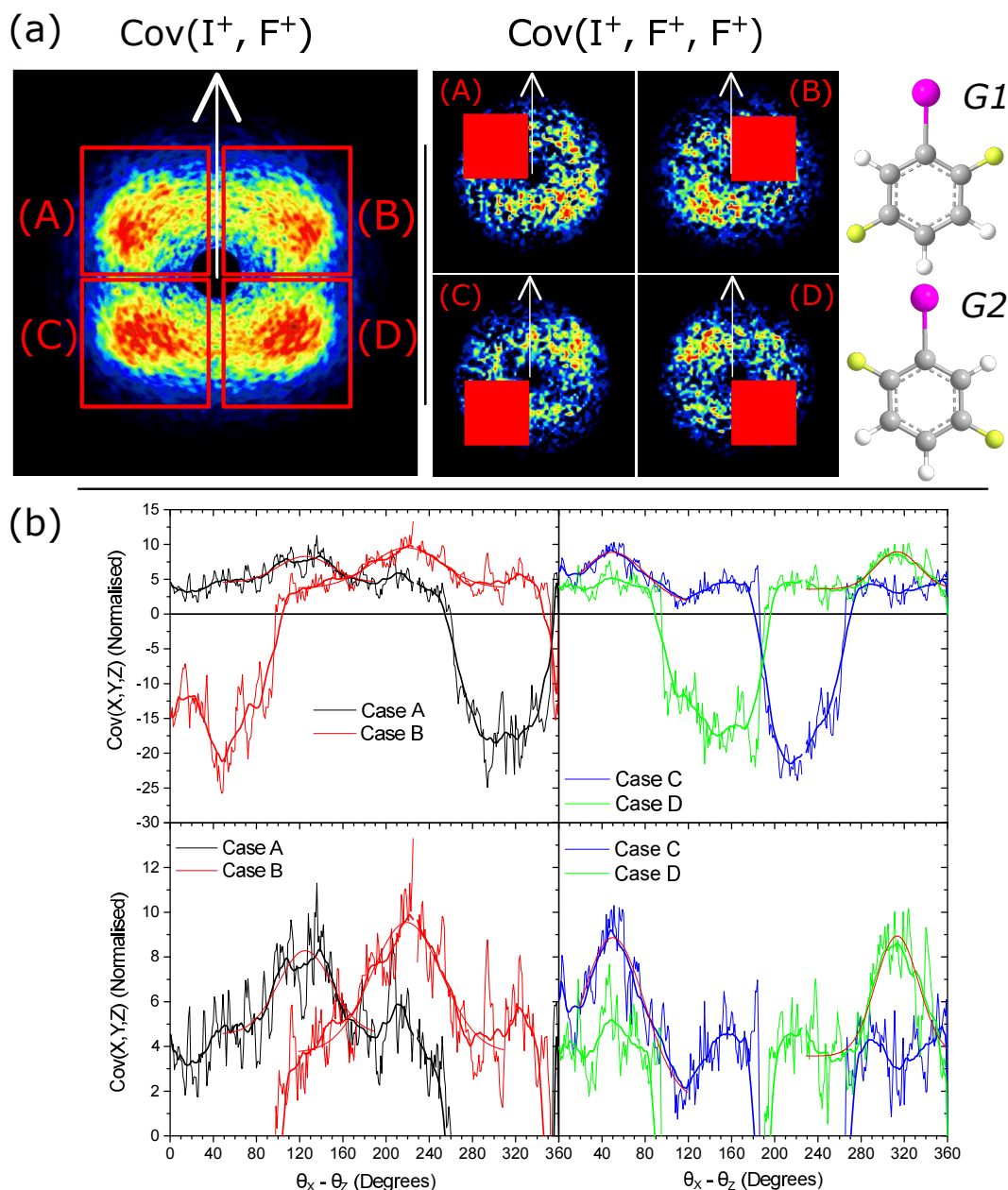


Figure 5.10: (a) The two-fold covariance map, $Cov(I^+, F^+)$, is shown on the left-hand side accompanied by four three-fold covariance maps, $Cov(I^+, F^+, F^+)$, on the right-hand side. In the former, I^+ and F^+ are the reference and plotted ions, while in the latter, I^+ is the reference ion, the first F^+ is the constrained ion and the second F^+ is the plotted ion. The constrained ion is restricted to the region indicated by the red squares and labelled as cases A, B, C, and D. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow. (b) The angular distribution of the corresponding three-fold covariance maps in panel (a) are shown for cases A (black trace), B (red trace), C (blue trace) and D (green trace). The angle $\theta_X - \theta_Z$ refers to the emission angle of the second F^+ ion relative to the reference ion, I^+ . Zoom-ins (bottom row) of the full distributions (top row) are also shown. The red thin lines correspond to Gaussian fits to each peak. Ball-and-stick models show the 2,5-DFIB molecule in two particular geometries, labelled G1 and G2, on the right side of panel (a).

emission of the two F^+ ions to each other, and so case A corresponds to ‘geometry 2’ (G2) of 2,5-DFIB (see ball-and-stick model labelled ‘G2’ in panel (a) of Figure 5.10).

The negative values above 250° suggest that I^+ and the two F^+ ions are uncorrelated, which correspond to the constrained region. The same trend is also observed in cases B (red trace), C (blue trace), and D (green trace) - *i.e.* the constrained ion (first F^+) is emitted at 180° with respect to the plotted ion (second F^+) - with the third ion of interest (*i.e.* the second F^+ ion) emitted at 219° , 50° , 313° relative to the reference ion I^+ , respectively. Therefore, cases B, C, and D correspond to the following geometries of 2,5-DFIB: G1, G1, and G2. In summary, both the two-fold and three-fold covariance maps support the conclusion that the data presented in Figure 5.8(d) and Figure 5.10 correspond to 2,5-DFIB.

Sections 5.3.2 and 5.3.3 have so far demonstrated that the identity of the structural isomers of DFIB can be determined just from the raw experimental data. It should also be noted that only a select few two- and three-fold covariance maps were required to identify the isomers of DFIB, even though a significant amount of information was recorded by the PImMS2 camera, as illustrated by the full covariance maps of all four DFIB molecules (in Figures A.1-A.4 of Appendix A). In the following section, an approximate simulation of the experimental results is carried out to investigate the accuracy of the Coulomb explosion simulation algorithm in reproducing the experimental results.

5.3.4 Simulation of Experimental Results

Simulations of the experimental results were generated through a classical many-body Coulomb explosion simulation, details of which have been given elsewhere [54], with only a brief description given here. In the simulation, approximately 50,000 molecules were generated with a Poisson distribution of charges. A mean total charge of +13 was used which gave the best match between the raw experimental data and the simulated data. A mean total charge of less than +13 lead to the break down of the axial recoil approximation. In this approximation, fragment ions are generated with velocities that are directly related to their position in the molecule before ionization occurs.

	3,5-DFIB	2,6-DFIB	2,4-DFIB	2,5-DFIB
H ⁺	0.69	0.78	0.75	0.71
C ⁺	0.38	0.42	0.41	0.40
C ²⁺	0.01	0.01	0.01	0.01
F ⁺	0.54	0.53	0.44	0.47
I ⁺	1.00	1.00	1.00	1.00
I ²⁺	0.35	0.36	0.32	0.32

Table 5.2: The integrated signal of the relevant fragments relative to I⁺ for the four structural isomers of DFIB investigated in this work.

Each atom is assigned a maximum charge state, with each charge state assigned a probability of generation by that particular charged ion. Both the maximum charge state and the probability of the various charge states of fragment ions are determined by a ToF analysis on the experimental ToF data. This analysis takes into account the integrated ToF signal for each ion fragment relative to I⁺, and are listed in Table 5.2. For example, the highest charge state of iodine generated in the experimental data for 3,5-DFIB was I²⁺, with the probabilities of 1.00 and 0.35 assigned to the +1 and +2 charge states of iodine, respectively. A probability of 1.00 indicates that this particular charged ion is formed in all molecules, while a probability of 0.35 refers to the charged ion being generated by only 35% of molecules.

In general, the simulated data presented earlier in Figure 5.8 agree well with the experimental data. The recoil angles in the simulated data appear at approximately the same recoil angles as in the experimental data. The biggest discrepancy between the simulated and experimental data is observed in the $Cov(F^+, F^+)$ maps for 3,5-DFIB. The discrepancy can be accounted for by considering the location of charge placed on the carbon atoms in the benzene ring, details of which are given in the next section.

5.3.5 Location of Charge on the Benzene Ring

The $Cov(C^+, H^+)$ and $Cov(I^+, C^+)$ maps, shown in Figure 5.11, are investigated to determine the location of charge on the benzene ring and hence which of the carbon atoms are ionized by the 800 nm pulse. In $Cov(C^+, H^+)$ map of 3,5-DFIB, the H⁺ ions are emitted at approximately 0°, 135° and 225° relative to C⁺. This corresponds to

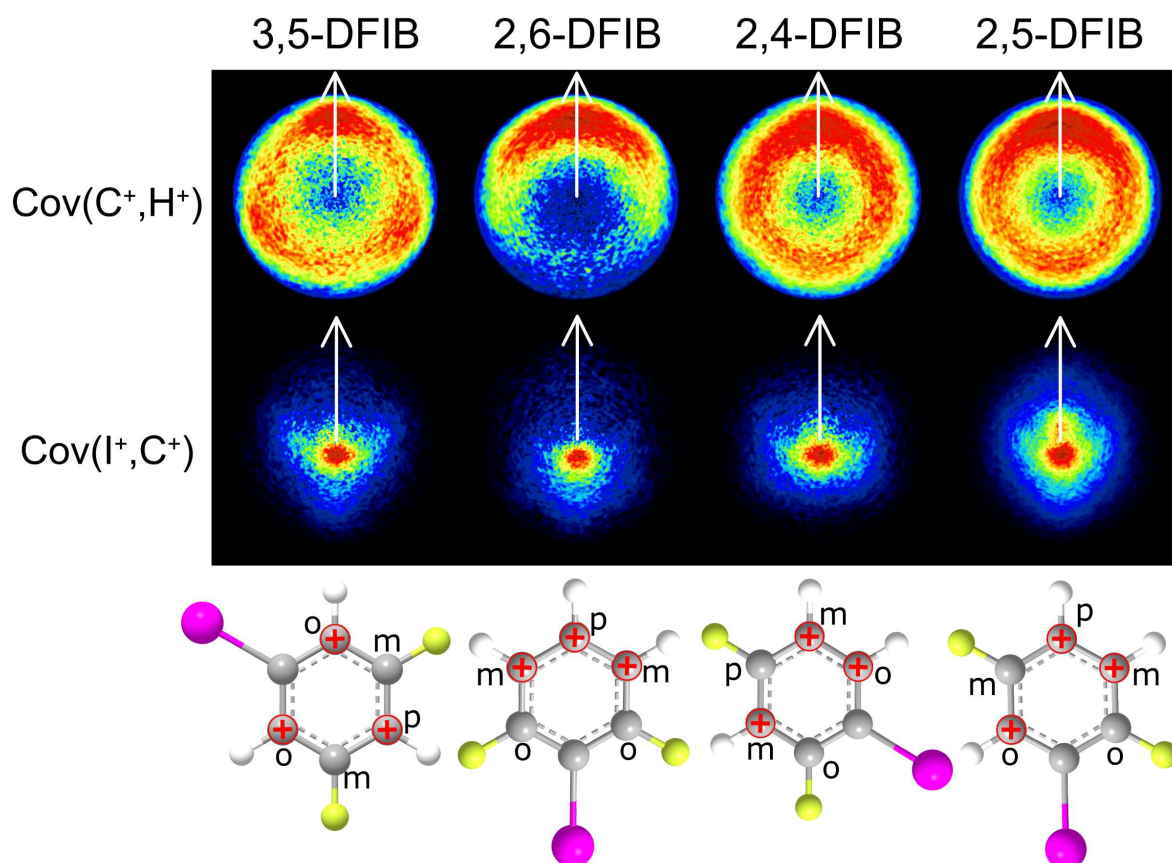


Figure 5.11: The two-fold covariance maps, $\text{Cov}(\text{C}^+, \text{H}^+)$ and $\text{Cov}(\text{I}^+, \text{C}^+)$, for the four isomers of DFIB. Positive charges (red crossed circles) are placed on the carbon atoms in the ball-and-stick models for each model (bottom row) based on the $\text{Cov}(\text{C}^+, \text{H}^+)$ maps.

the detection of C^+ ions correlated with H^+ ions that are either at the same position on the benzene ring, since they both fly in the same (forward) direction, or the H^+ ions are at a meta position relative to the C^+ reference ion. In the $\text{Cov}(\text{I}^+, \text{C}^+)$ map, the C^+ ions are emitted back-to-back (ortho) to the I^+ reference ion. Thus, the charge on the carbon atoms is located at the ortho and para positions relative to the iodine atom, as shown by the ball-and-stick model below the covariance maps in Figure 5.11.

A similar effect has been observed by Rolles and coworkers in the inner-shell ionization of unaligned 3,5-DFIB molecules [291]. The kinetic energy distributions (KEDs) and $\text{I}^+ - \text{F}^+$ emission angles extracted from their electron-ion-ion coincidence measurements for the $\text{I}^+ + \text{C}_6\text{H}_3\text{F}_2^+$ and $\text{I}^+ + \text{C}_6\text{H}_3\text{F}_2^{2+}$ fragmentation channels were compared to Coulomb explosion two-body and three-body simulations [291]. In their simulations, they considered the charge on the benzene ring at three locations: on the carbon closest to the iodine atom, in the middle of the benzene ring, and on the carbon furthest

away from the iodine atom. The authors found that the distance of 491 pm between I^+ and C^+ gave the best match between the measured and simulated KEDs and emission angles. This distance corresponds to the charge on the benzene ring being placed as far away from the iodine atom in the molecule as possible (*i.e.* para to the iodine) [291]. The authors proposed the following possible mechanism to explain this effect: the inner-shell ionization of the molecule leads to the ejection of an electron from the 4d shell of iodine. The vacancy in the core shell is rapidly filled by an Auger decay process, which leads to the ejection of a second and possibly third electron from the valence molecular orbitals. The two or three holes, which are initially strongly localized on the iodine site of the molecule, repel each other such that charge migration in the molecule may lead to the holes being located on opposite sides of the ring to each other in the molecule before its Coulomb explosion occurs, minimizing the repulsive forces that exist between the holes.

In the data presented in Figure 5.11, the strong-field ionization of the molecule leads to the ejection of one or more electrons from the valence (and not the core) orbital of the molecule. Therefore, in the strong-field case, the charges on the carbon atoms in the molecule will already be well-separated. This is somewhat different to the inner-shell case, where the initial charge is strongly localized on the iodine site of the molecule before charge migration occurs, which could lead to the holes being located at different positions in the benzene ring than in the strong-field case. The difference between the two ionization schemes may account for why the charge on the carbon atoms was not also observed to be para to the iodine atom in the inner-shell ionization study by Rolles and coworkers [291]. However, it should be noted that a second contribution to the KED of the $I^+ + C_6H_3F_2^{2+}$ fragmentation channel was observed by Rolles and coworkers [291], with the best match to the simulated data found to be with the charge on the benzene ring placed in the middle of the ring.

Since the charges on the benzene ring are ortho and para to the iodine atom in 3,5-DFIB, as illustrated by the ball-and-stick model in Figure 5.11, the carbon charges are close enough to the F^+ ions such that they can repel the two F^+ ions towards each other. This could explain the smaller angle of 106° extracted from the $Cov(F^+, F^+)$

map than the expected angle of 120° .

In the $Cov(C^+, H^+)$ map of 2,6-DFIB, the H^+ ions are emitted in the same (forward) direction as the C^+ reference ions. This suggests that the charge on the benzene ring is placed as far away as possible from the I^+ and F^+ ions. The $Cov(I^+, C^+)$ map shows a back-to-back emission of C^+ ions relative to I^+ ions. This effect was also observed in the inner-shell ionization of 2,6-DFIB by Rolles and coworkers [291], with the charge on the benzene ring found to be as far away from the iodine atom as possible. In 2,4-DFIB and 2,5-DFIB, the H^+ ions are emitted at a broad range of angles relative to C^+ , but both molecules have the most intense signal at approximately 0° . Just as in the 3,5-DFIB and 2,6-DFIB isomers, the $Cov(I^+, C^+)$ maps in 2,4-DFIB and 2,5-DFIB also show a back-to-back emission of C^+ ions relative to I^+ .

The experimental covariance maps for the four isomers of DFIB have been successfully used to determine the location of charge on the benzene as well as identify each structural isomer of DFIB. These experimental covariance maps for the pure structural isomers of DFIB will be used in the following section to identify and determine the abundance of the isomers present in a measurement that uses a mixture of two isomers.

5.4 Identification of DFIB Isomers in a Mixture

As discussed previously, it was impossible to distinguish the identity of the isomers present in the mixture measurement just from the ToF and ion images. By comparing the two-fold covariance map for the mixture, shown in Figure A.5 in Appendix A, to the corresponding maps for the pure isomers shown in Section 5.3, the identity and ratio of the isomers present in the mixture can be determined. The most significant two-fold covariance maps for the mixture are presented in Figure 5.12 with a detailed discussion given in the following section.

5.4.1 Identification of Isomers

The experimentally obtained covariance maps from the mixture measurement are shown in the first row of Figure 5.12. The second row shows the sum of the covariance maps

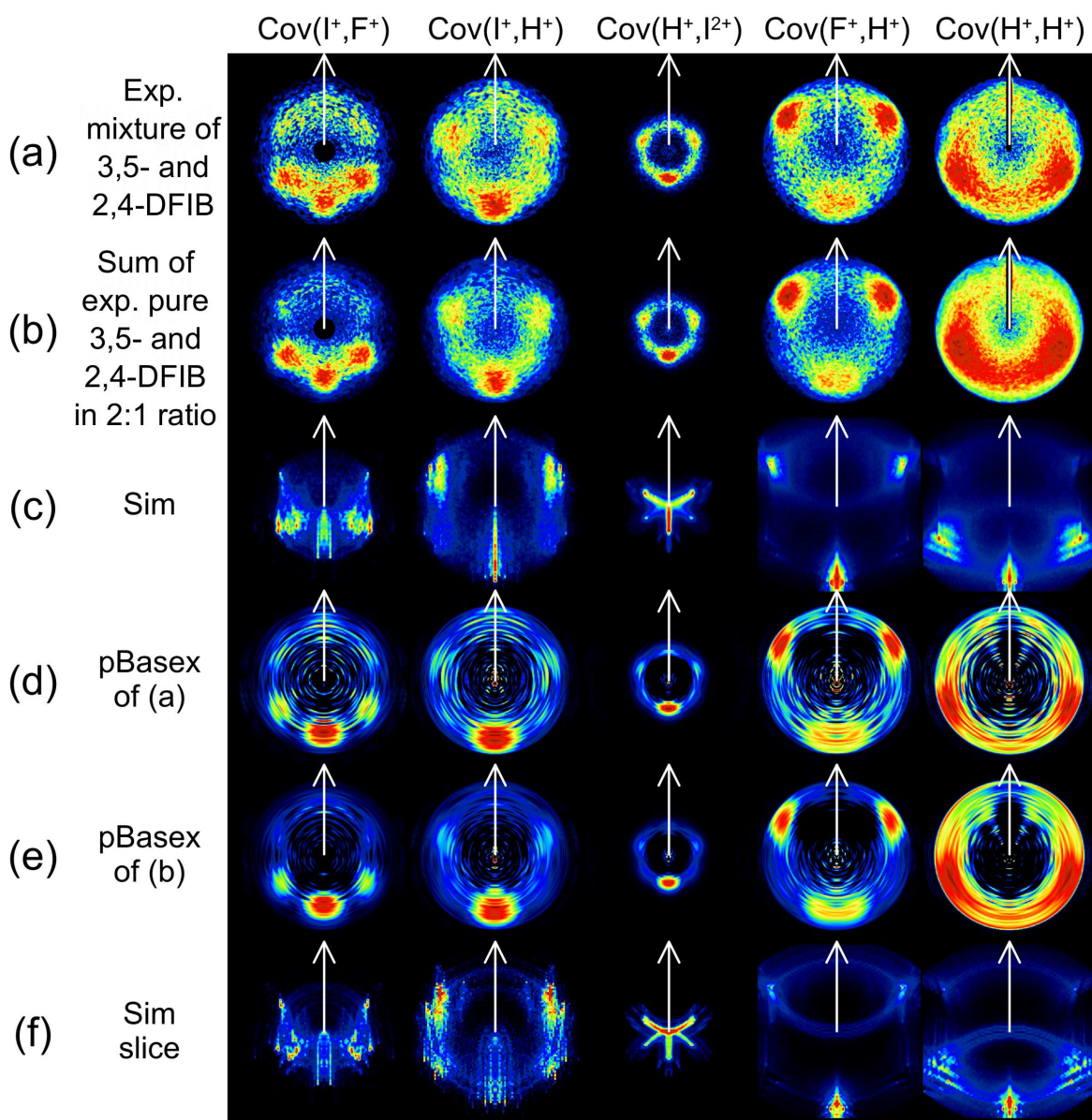


Figure 5.12: Two-fold covariance maps, $Cov(X, Y)$, are presented for a mixture of 1D-aligned 3,5- and 2,4-DFIB molecules. The six rows are: (a) the experimental mixture data, (b) the sum of experimental data for pure 3,5- and 2,4-DFIB isomers in a 2:1 ratio, (c) the simulated data, (d) pBasex-inversion of (a), (e) pBasex-inversion of (b), and the central slice distribution of the simulated data. Each column presents a two-fold covariance map, $Cov(X, Y)$, with the reference ion denoted as X and the plotted ion denoted as Y . The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow.

corresponding to the 3,5- and 2,4-DFIB pure isomers in a 2:1 ratio, and is accompanied by the corresponding simulated data in the third row of images. There is very good qualitative agreement between the first three rows of images.

In the 3,5-DFIB isomer, the F^+ ions are emitted at approximately 120° and 240° relative to I^+ , and are clearly present in the $Cov(I^+, F^+)$ mixture map in panel (a),

while in the 2,4-DFIB isomer, the F^+ ion has a strong back-to-back emission with I^+ as well as two weaker emissions at approximately 70° and 290° . The back-to-back emission in the $Cov(I^+, F^+)$ map is unique to the 2,4-DFIB isomer, and is also clearly visible in the $Cov(I^+, F^+)$ mixture map in panel (a). The emission of F^+ at 70° and 290° relative to I^+ in the pure 2,4-DFIB isomer is difficult to identify in both the mixture and summed $Cov(I^+, F^+)$ maps.

It should also be noted that 2,4-DFIB was the first molecule that was studied which was followed by the mixture of 3,5- and 2,4-DFIB, and so no trace of 2,6-DFIB or 2,5-DFIB isomers could be present in the mixture measurement. The absence of any significant features in the top-half of the $Cov(I^+, F^+)$ mixture map confirms the absence of the 2,5-DFIB and 2,6-DFIB isomers in the mixture.

The $Cov(I^+, H^+)$ maps show a very good qualitative agreement between the mixture and summed pure experimental data, as shown in panels (a) and (b) of Figure 5.12. The corresponding simulated data in panel (c) also agrees with the experimental data, although the former is better resolved than the latter. In all three data sets, the H^+ ions are emitted ortho, meta and para to the I^+ ions, which is consistent with the presence of both 3,5-DFIB and 2,4-DFIB in the mixture. In the remaining three columns of maps, similar features are seen in both the mixture and summed maps, although interestingly, the $Cov(H^+, H^+)$ map in the mixture measurement is less intense than in the sum of the pure data. Slice images were generated following the pBasex-inversion of the maps in panels (a) and (b), and are shown in panels (d) and (e). These are accompanied by the slice image from the simulated data as shown in panel (f). A good qualitative agreement is also seen in all three sets of slice images.

5.4.2 Abundance of Isomers

To quantify the ratio of 3,5-DFIB and 2,4-DFIB isomers present in the mixture measurement, the angular distribution of the mixture data was compared to the summed data using their raw and pBasex-inverted data as shown in Figure 5.13(a) and (b), respectively. In both panels, the angular distribution of the summed data is shown for the following 3,5-DFIB:2,4-DFIB ratios: 1:1 (blue trace), 2:1 (black trace), and the

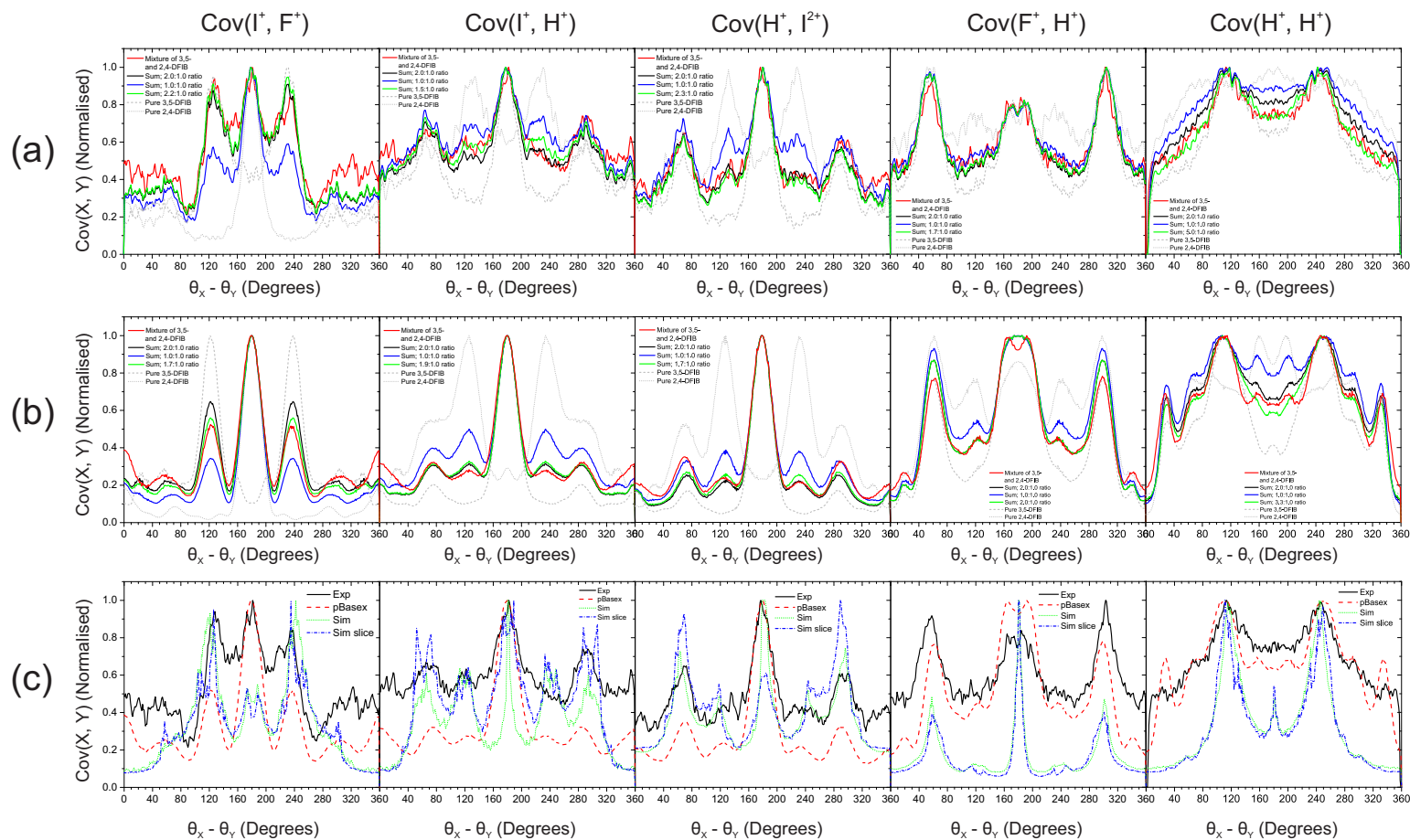


Figure 5.13: Angular distributions of two-fold covariance maps for (a) raw experimental data and (b) pBasex-inverted data. The distributions in panels (a) and (b) correspond to the experimental mixture data (red solid trace), the pure 3,5-DFIB and 2,4-DFIB experimental data (grey dash and grey dotted traces, respectively), and the sum of the two pure isomer experimental data in a 1.0:1.0 (blue trace), 2.0:1.0 (black trace) and some optimal (green trace) 3,5-DFIB:2,4-DFIB ratio. (c) Comparison of the mixture data, with the distributions corresponding to the raw experimental mixture crushed data (black solid trace), the pBasex slice data (red dash trace), the simulated crushed data (green dotted trace), and the simulated slice data (blue dashed-dotted traces).

ratio that gives the best match (green trace) to the corresponding mixture (red trace). The distributions for the pure 3,5-DFIB and 2,4-DFIB isomers are also shown. All distributions are normalised to their corresponding maximum intensity. Table 5.3 lists the ratio used in the summed data that best matches the mixture distribution for both the experimental and pBasex-inverted data. In all two-fold covariance maps, the summed distribution with a 2:1 ratio shows a better match with the mixture distribution than the corresponding summed distribution that used a 1:1 ratio.

For example, in the $Cov(I^+, F^+)$ map, the ratio of 2.2:1.0 and 1.7:1.0 gives the best match between the mixture and summed data in their raw experimental and pBasex distributions, respectively. While in the $Cov(H^+, H^+)$ map, a ratio of 5.0:1.0 and 3.3:1.0 was obtained from the raw experimental and pBasex data, respectively, which is significantly different to the approximate 2:1 ratio seen in all other covariance maps. The average ratio from all five covariance maps is $2.5 \pm 1.4:1.0$ and $2.1 \pm 0.7:1.0$ for the raw experimental and pBasex data, respectively, with the error taken as the standard deviation of the five 3,5-DFIB:2,4-DFIB ratios.

If the result from the $Cov(H^+, H^+)$ map is ignored, the uncertainty in both average ratio values is significantly improved to give $1.9 \pm 0.4:1.0$ and $1.8 \pm 0.2:1.0$ for the raw experimental and pBasex data, respectively. Thus, for every 2,4-DFIB molecule there exist approximately two molecules of 3,5-DFIB in the mixture measurement. Figure 5.13(c) shows the raw experimental and pBasex angular distributions for the mixture data along with the corresponding simulated data. The recoil angles were extracted from the pBasex distributions as a sum of Gaussians and are listed in Table 5.1.

Overall, the recoil angles extracted from the mixture data correspond to the 2,4-DFIB and 3,5-DFIB molecules. For example, the $Cov(I^+, F^+)$ map shows that F^+ ions were ejected with the following recoil angles with respect to I^+ : 124° , 235° , 55° , 180° , 305° . The former two angles correspond to 3,5-DFIB, while the final three angles originate from 2,4-DFIB.

In the following section, the effect of substituting the fluorine atoms for hydroxy (OH) groups is investigated. Firstly, the isomers of DHBB will be identified through their two- and three-fold covariance maps, followed by a comparison between DFIB and DHBB.

	$Cov(I^+, F^+)$	$Cov(I^+, H^+)$	$Cov(H^+, I^{2+})$	$Cov(F^+, H^+)$	$Cov(H^+, H^+)$
Exp	2.2:1.0	1.5:1.0	2.3:1.0	1.7:1.0	5.0:1.0
pBasex	1.7:1.0	1.9:1.0	1.7:1.0	2.0:1.0	3.3:1.0

Table 5.3: The optimum 3,5-DFIB:2,4-DFIB ratios as determined from the angular distributions (green traces) of the raw experimental and pBasex data shown in Figure 5.13.

An attempt to identify the conformers that are present in the DHBB measurements, due to the stabilising bromine-hydrogen interactions, is made through a comparison of simulated data with the experimental results.

5.5 Identification of DHBB Isomers

In this section, the Coulomb explosion of bromohydroquinone (2,5-DHBB) and 2-bromoresorcinol (2,6-DHBB) molecules is carried out, using the same experimental set-up as for the DFIB measurements, to investigate the feasibility of detecting hydroxy, OH^+ , ions in coincidence with Br^+ ; analogous to detecting F^+ ions with I^+ in DFIB. This study serves as a test case for possible future experiments on biologically relevant molecules that contain hydroxy substituent groups, such as carbohydrates and amino acids [292].

5.5.1 ToF Spectra and Ion Images

Figure 5.14 shows the ToF distributions for unaligned (solid traces) and 1D-aligned (dashed traces) 2,6-DHBB (black traces) and 2,5-DHBB (blue traces) molecules. Above the ToF traces are the ion images corresponding to the shaded ToF profiles (H^+ , OH^+ , Br^{2+} , and Br^+). The alignment pulse fragments the large molecular ions into atomic and small molecular fragments (see Section 5.6 for an insight into the effect of the alignment pulse).

The OH^+ ion images for the two isomers of DHBB look different to the corresponding F^+ ion images in DFIB, with the OH^+ ions in DHBB ejected with a recoil angle that is not as distinct as the F^+ ions in DFIB. This makes the two-fold covariance technique

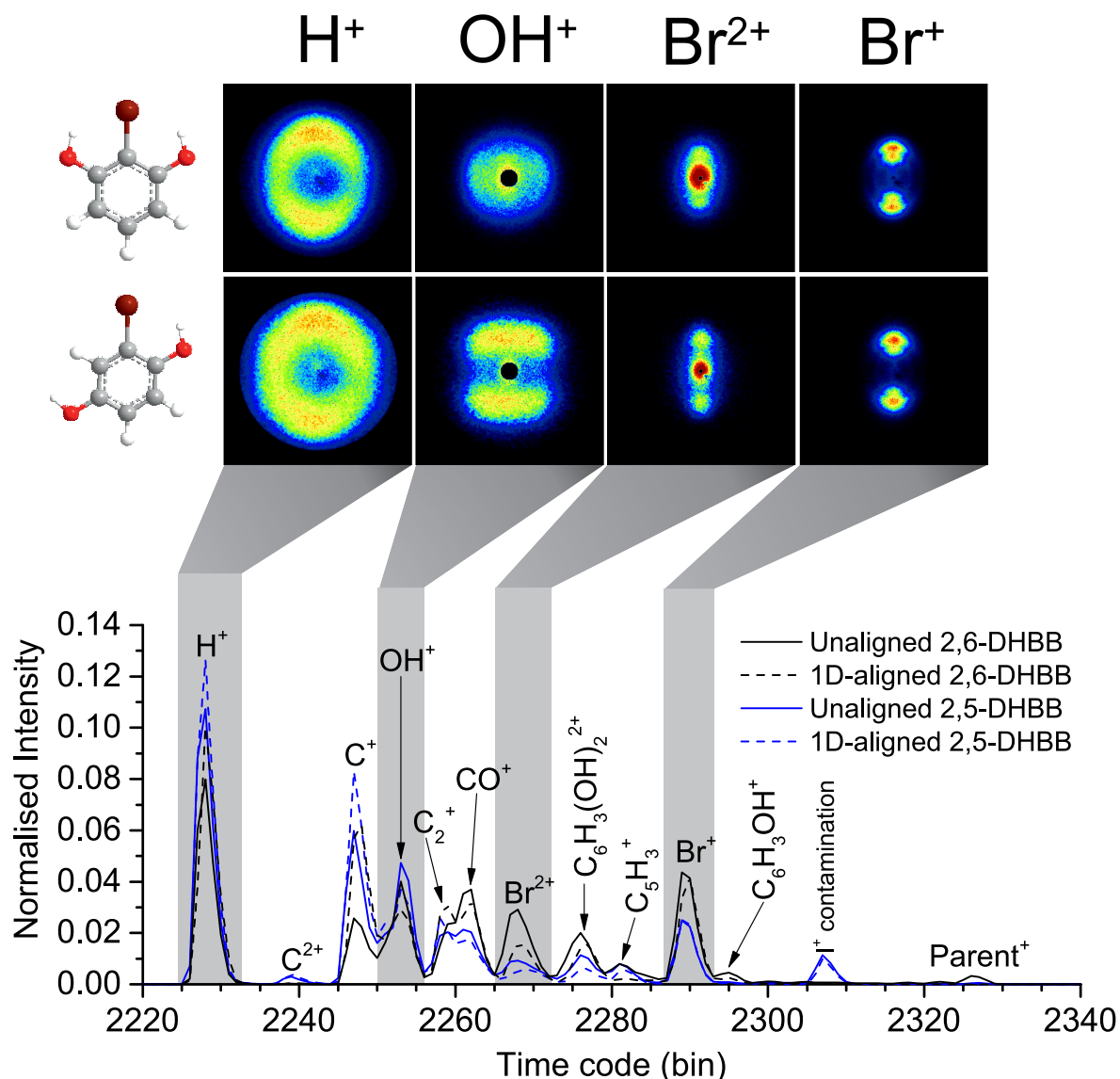


Figure 5.14: Time-of-flight spectra recorded by the PImMS2 camera for 1D-aligned DHBB molecules following strong-field ionization with an intense 800 nm pulse polarized parallel to the detector plane. Measurements for 2,6- (black trace), and 2,5- (blue trace) pure isomers of DHBB are shown. The corresponding laboratory-frame ion images are shown above the assigned time-of-flight peaks for the most significant ion fragments (H^+ , OH^+ , Br^{2+} , and Br^+). The grey shading indicates the time-of-flight range used to generate each ion image.

even more crucial to identify the isomers of DHBB that were recorded. The H^+ ions generated from DHBB are similar to the those of DFIB, although its features in the H^+ ion image for the DHBB molecule are not as distinct as in the DFIB molecule. The Br^+ ion images show pronounced confinement along the alignment pulse polarization axis. Determination of $\langle \cos^2 \theta_{2D} \rangle$ gives 0.89, confirming strong alignment of the C-Br axis along the laser polarization.

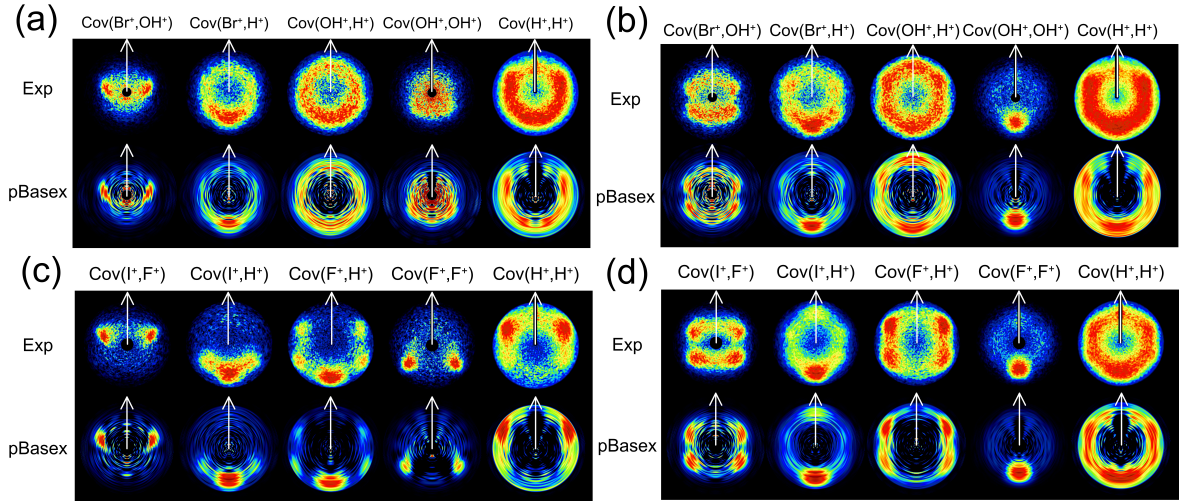


Figure 5.15: Selected two-fold recoil-frame covariance maps, $Cov(X,Y)$, of 1D-aligned: (a) 2,6-DHBB, (b) 2,5-DHBB, (c) 2,6-DFIB and (d) 2,5-DFIB. The two rows in each panel correspond to the raw experimental crushed data (top row) and the pBasex slice data (bottom row). Each column presents a two-fold covariance map, $Cov(X,Y)$, with the reference ion denoted as X and the plotted ion denoted as Y . The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map.

The two-fold covariance maps for 1D-aligned and unaligned data are shown for 2,6-DHBB in Figure A.8 and for 2,5-DHBB in Figure A.9, both in Appendix A.

5.5.2 Identification of Structural Isomers

The five most significant two-fold covariance maps for 2,6-DHBB and 2,5-DHBB are shown in Figure 5.15(a) and (b), which are: $Cov(Br^+, OH^+)$, $Cov(Br^+, H^+)$, $Cov(OH^+, H^+)$, $Cov(OH^+, OH^+)$, and $Cov(H^+, H^+)$. These are accompanied by the analogous maps for 2,6-DFIB and 2,5-DFIB in panels (c) and (d), which are: $Cov(I^+, F^+)$, $Cov(I^+, H^+)$, $Cov(F^+, H^+)$, $Cov(F^+, F^+)$, and $Cov(H^+, H^+)$. In each panel, the raw experimental data (top row) and pBasex-inverted data (bottom) are shown.

The angular distributions extracted from the maps in Figure 5.15 are presented in Figure 5.16. The angular distributions of the pBasex data are clearly better resolved than the corresponding raw experimental data, particularly in the $Cov(OH^+, OH^+)$ map of 2,6-DHBB. Therefore, the recoil angle of the plotted ion relative to the reference ion was extracted from the pBasex data by fitting a sum of Gaussians to the pBasex

angular distributions. The recoil angles, taken as the mid-point of each Gaussian fit, are listed in Table 5.4. In the following discussion, the raw experimental data will be used to determine the identity of the DHBB isomers present in the data presented in panels (a) and (b) of Figure 5.15.

In panel (a) of Figure 5.15, the $Cov(Br^+, OH^+)$ experimental map contains two local maxima features. In this map, the OH^+ ions are ejected at 85° and 275° relative to the Br^+ ion, and so the hydroxy group must occupy the ortho positions (relative to bromine) on the benzene ring. The OH^+ ions in the $Cov(OH^+, OH^+)$ map are ejected at approximately 130° and 230° to each other. This confirms that two hydroxy groups occupy the ortho positions (relative to bromine) on the benzene ring as opposed to only one hydroxy group, since the latter case would not have shown any positive intensity signal in the $Cov(OH^+, OH^+)$ two-fold covariance map.

The H^+ ions in the $Cov(Br^+, H^+)$ experimental map are ejected at five recoil angles relative to the Br^+ ion, which suggests that the hydrogen atoms occupy the ortho, meta and para positions of the molecule. It has already been shown that the hydroxy group is present at the ortho position, and so therefore the two H^+ ions that appear ortho to Br^+ in the $Cov(Br^+, H^+)$ must have originated from the hydroxy group. Thus, these three covariance maps have clearly demonstrated that the data presented in panel (a) of Figure 5.15 correspond to 2,6-DHBB.

In panel (b) of Figure 5.15, a four-fold feature is observed in the $Cov(Br^+, OH^+)$ map, which has also been previously observed in the $Cov(I^+, F^+)$ map for 2,5-DFIB (see Sections 5.3.2 and 5.3.3). The four-fold feature suggests that the hydroxy groups occupy the ortho and meta positions of the molecule. In the $Cov(OH^+, OH^+)$ map, a localized feature at 180° is observed which confirms that two hydroxy groups must exist in the molecule, one at the ortho position and the second at the meta position, with both back-to-back to each other. Thus, just from these two maps, it can be concluded that the data in panel (b) corresponds to 2,5-DFIB. To further confirm this assignment and to investigate the origin of the four-fold feature in the $Cov(Br^+, OH^+)$ map of 2,5-DHBB, the three-fold covariance map $Cov(Br^+, OH^+, OH^+)$ was calculated, details of which are given in the following section.

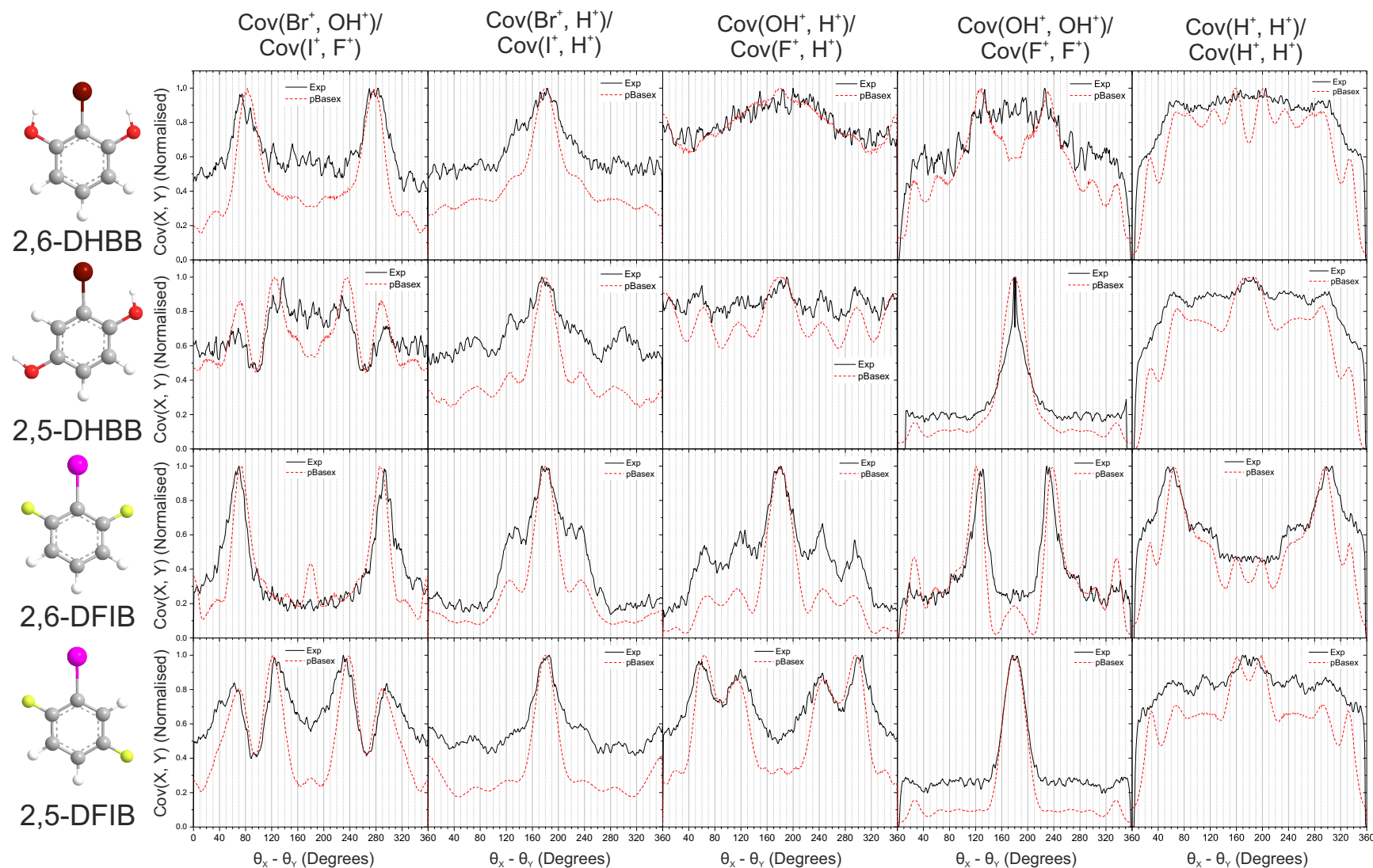


Figure 5.16: Angular distributions extracted from the two-fold covariance maps in Figure 5.15. The distributions for the raw experimental crushed data (black solid trace) and pBasex slice data (red dashed trace) are shown. Each distribution has been normalised to its maximum intensity to facilitate comparison.

	$Cov(Br^+, OH^+)$	$Cov(Br^+, H^+)$	$Cov(OH^+, H^+)$	$Cov(OH^+, OH^+)$	$Cov(H^+, H^+)$
2,6-DHBB	84.7(4)°, 275.3(4)°	75.1(5)°, 130.9(3)°, 180.0(1)°, 229.1(3)°, 284.9(5)°	4.3(15)°, 65.4(3)°, 140.5(56)°, 180.0(2)°, 224.1(56)°, 288.3(3)°	129.9(9)°, 227.9(9)°	124.0(3)°, 159.3(2)°, 200.0(2)°, 234.9(3)°
2,5-DHBB	74.6(5)°, 126.0(2)°, 234.0(3)°, 285.3(6)°	72.8(3)°, 124.6(2)°, 180.0(1)°, 235.4(2)°, 287.2(3)°	5.7(19)°, 62.0(10)°, 117.0(23)°, 180.0(7)°, 243.0(23)°, 298.0(10)°	179.3(1)°	65.3(5)°, 103.8(8)°, 179.6(3)°, 255.1(7)°, 295.2(5)°

Table 5.4: Angle of recoil extracted from the two-fold $Cov(X, Y)$ covariance maps following pBasex-inversion of 2,6-DHBB and 2,5-DHBB experimental data shown in Figure 5.15. The error in the recoil angles is given by the values in the brackets and corresponds to the fitting error.

5.5.3 Three-fold Covariance of 2,5-DHBB

The $Cov(Br^+, OH^+, OH^+)$ three-fold covariance map, shown in Figure 5.17, had the Br^+ ion selected as the reference ion, one of the OH^+ restricted to the region indicated by the filled red square, and the second OH^+ ion plotted in the recoil-frame of the Br^+ reference ion. Each of the four features in the two-fold $Cov(Br^+, OH^+)$ map is marked by red squares, shown in panel (a), and were subsequently used as the four constrained regions in the $Cov(Br^+, OH^+, OH^+)$ three-fold covariance maps shown on the right hand-side of panel (a) (filled red squares).

In case A, the second OH^+ (plotted) ion is ejected at approximately 150° to the Br^+ (reference) ion. Therefore, the first OH^+ is emitted back-to-back to the second OH^+ ion, and so case A corresponds to ‘geometry 2’ (G2) of 2,5-DHBB (see ball-and-stick model labelled ‘G2’ in panel (a) of Figure 5.17). In the same three-fold map, negative values are observed above 250° , corresponding to the constrained region, suggesting that Br^+ and the two OH^+ ions are uncorrelated.

The same trend is also seen in cases B (red trace), C (blue trace), and D (green trace) - *i.e.* the constrained ion (first OH^+) is emitted at 180° with respect to the plotted ion (second OH^+) - with the third ion of interest (*i.e.* the second OH^+ ion) emitted at approximately 215° , 60° , 320° relative to Br^+ , respectively. Therefore, cases B, C, and D correspond to the following geometries of 2,5-DHBB: G1, G1, and G2. In summary, both the two-fold and three-fold covariance maps support the conclusion that the data presented in Figures 5.15(d) and 5.17 correspond to 2,5-DHBB. Several similarities and differences exist between the 2,5- and 2,6- isomers of DHBB and DFIB, details of which are given in the following section.

5.5.4 Comparison of DHBB and DFIB Structural Isomers

The molecular ion peak in the ToF spectra without the YAG alignment pulse can be used to distinguish DFIB and DHBB ($m/q(DFIB^+) = 239.98$ and $m/q(DHBB^+) = 189.00$). To distinguish between the structural isomers of both DFIB and DHBB, a comparison between their respective covariance maps must be made. Firstly, the two-

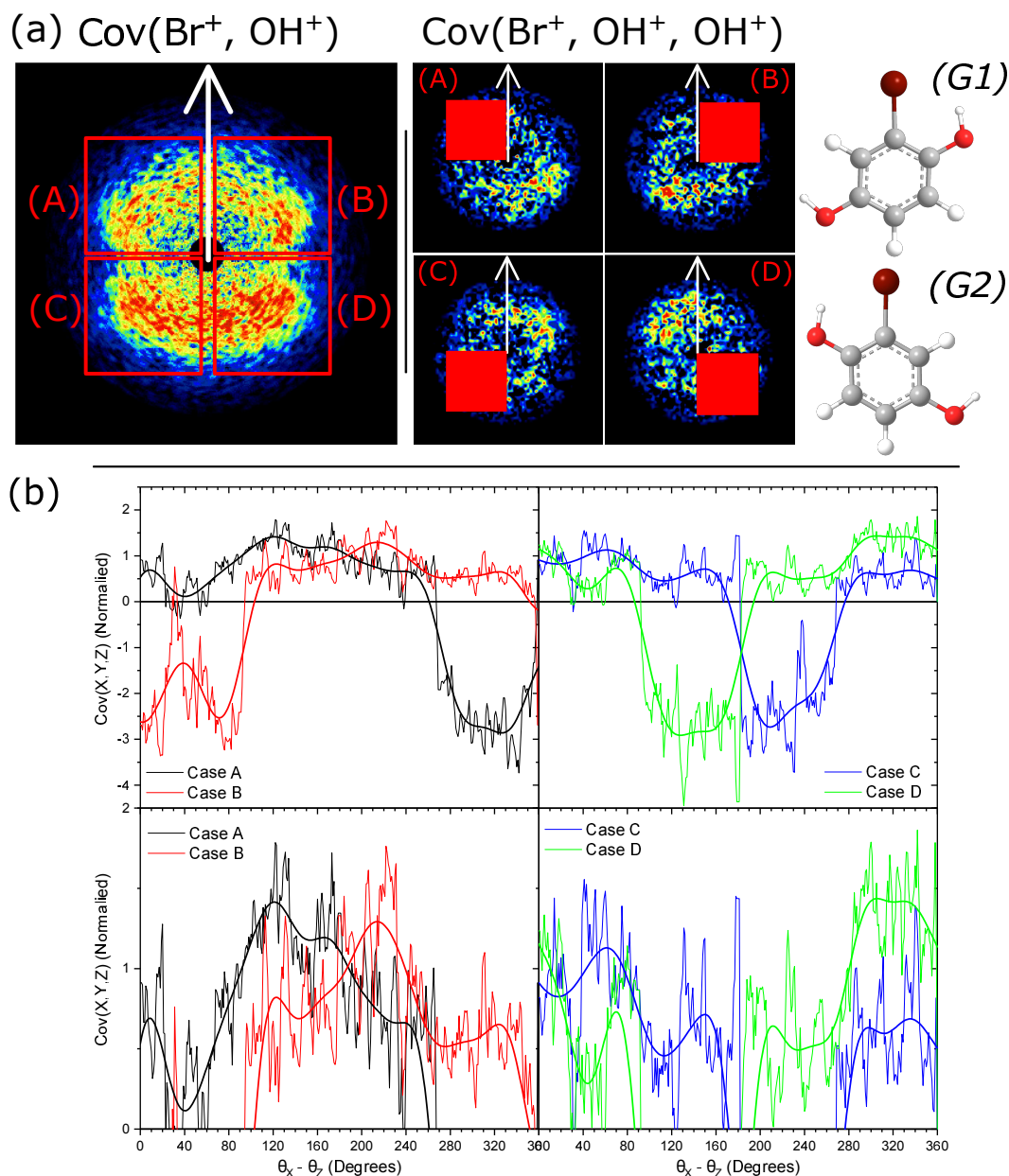


Figure 5.17: (a) The two-fold covariance map, $Cov(Br^+, OH^+)$, is shown on the left-hand side accompanied by four three-fold covariance maps, $Cov(Br^+, OH^+, OH^+)$, on the right-hand side. In the former, Br^+ and OH^+ are the reference and plotted ions, while in the latter, Br^+ is the reference ion, the first OH^+ is the constrained ion and the second OH^+ is the plotted ion. The constrained ion is restricted to the region indicated by the red squares and labelled as cases A, B, C, and D. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow. (b) The angular distribution of the corresponding three-fold covariance maps in panel (a) are shown for cases A (black trace), B (red trace), C (blue trace) and D (green trace). The angle $\theta_X - \theta_Z$ refers to the emission angle of the second OH^+ ion relative to the reference ion, Br^+ . The two panels on the bottom are blow-ups of the panels above. Zoom-ins (bottom row) of the full distributions (top row) are also shown. Ball-and-stick models show the 2,5-DHBB molecule in two particular geometries, labelled G1 and G2, on the right side of panel (a).

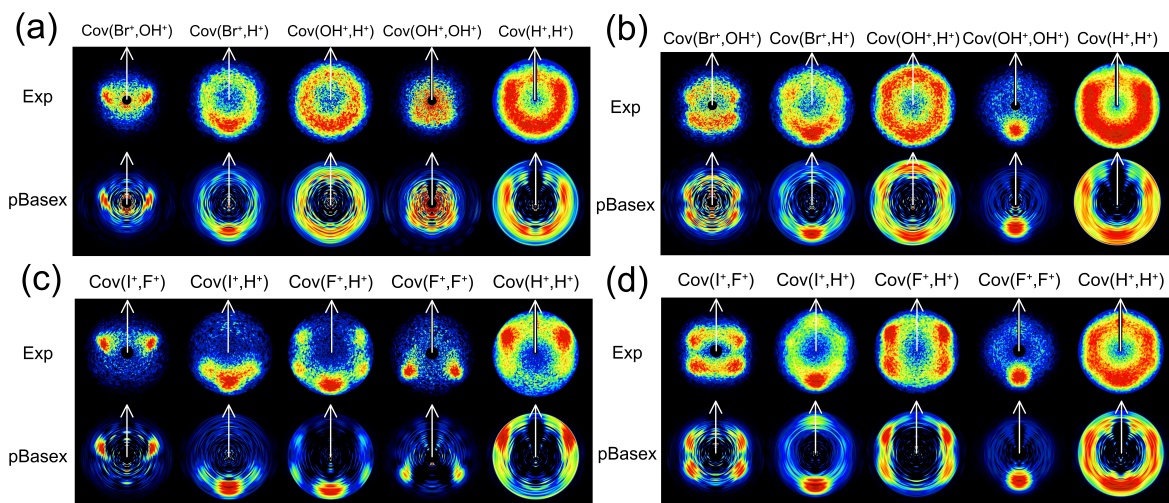


Figure 5.18: Identical to Figure 5.15, but also shown in this section for the reader's benefit.

fold covariance maps of 2,6-DHBB are compared to the analogous maps of 2,6-DFIB.

I. 2,6-DHBB vs. 2,6-DFIB

Substitution of the iodine and fluorine atoms with the bromine atom and the hydroxy group in the 2,6- isomer did not lead to significant differences in their $Cov(Br^+, OH^+)$ map - the OH^+ ions are ortho to the I^+ reference ion (see panels (a) and (c) of Figure 5.18). Although the $Cov(OH^+, OH^+)$ is not as well resolved as the $Cov(F^+, F^+)$ map, they both show that the first OH^+ (F^+) ion is ejected meta to the second OH^+ (F^+) ion. The most significant effect of substituting the hydroxy groups for the fluorines is seen in the $Cov(H^+, H^+)$, $Cov(Br^+, H^+)$ and $Cov(OH^+, H^+)$ maps.

In the $Cov(H^+, H^+)$ map of 2,6-DHBB, H^+ ions are ejected at nearly all angles relative to each other, which was not the case in 2,6-DFIB. In 2,6-DFIB, the H^+ ions were only emitted ortho or meta and not para (*i.e.* 180°) to each other. This is because in 2,6-DFIB, the fluorine and iodine atoms were placed at 180° to the H^+ ion. While in the 2,6-DHBB case, the rupturing of the O-H bond by the 800 nm pulse can lead to the emission of H^+ ions para (*i.e.* 180°) to each other, and subsequently leads to the “horseshoe” feature in the $Cov(H^+, H^+)$ map of 2,6-DHBB, which does not exist in the $Cov(H^+, H^+)$ map of 2,6-DFIB.

In the $Cov(Br^+, H^+)$ shown in Figure 5.18(a), the H^+ ions are ejected at five recoil angles relative to the Br^+ ion, which is two more than in the corresponding $Cov(I^+, H^+)$

map of 2,6-DFIB (see panel (c) of Figure 5.18). This corresponds to the appearance of hydrogen atoms at the ortho, meta and para positions of the molecule. The two additional features at 75° and 289° are assigned as belonging to the hydrogen atom from the hydroxy group following the rupturing of the O-H bond by the 800 nm pulse. Therefore, the 800 nm probe pulse can fragment the O-H group in some molecules to generate H^+ ions that are located around the ortho position of the molecule.

In the $Cov(OH^+, H^+)$ map, H^+ ions are ejected in the same (forward) direction as the OH^+ reference ion. This provides further evidence that the O-H group can be fragmented by the 800 nm pulse. It also shows that the ToF peak that was assigned as the OH^+ ion could contain contributions from the O^+ ion since the PImMS2 camera does not have the resolving power to resolve O^+ and OH^+ ToF peaks within the timing precision of 40 ns that was available at the time of the experiments. This would therefore explain the forward emission of O^+ and H^+ ions in the covariance map.

II. 2,5-DHBB vs. 2,5-DFIB

The biggest effect of hydroxy substitution on the 2,5- isomer is illustrated in the $Cov(OH^+, H^+)$ map. In the $Cov(OH^+, H^+)$ map of 2,5-DHBB, as shown in Figure 5.18(b), the H^+ ions are ejected at six distinct recoil angles relative to OH^+ ions, two more than in the analogous $Cov(F^+, H^+)$ map of 2,5-DFIB. This is also due to the fragmentation of the O-H group by 800 nm pulse, which generates O^+ and H^+ ions similar to the 2,6- case. Thus, the fragmentation of the O-H group accounts for the two additional recoil angles at 0° and 180° in the $Cov(OH^+, H^+)$, which is not present in the $Cov(F^+, H^+)$ map of 2,5-DFIB.

Although no significant differences are observed in the $Cov(Br^+, OH^+)$ map following the hydroxy substitution, the $Cov(Br^+, OH^+)$ map is not as well resolved as the $Cov(I^+, F^+)$ map. The four-fold feature present in both maps suggests that the OH^+ (F^+) ions are ejected ortho and meta to the Br^+ (I^+) reference ion. Hydroxy substitution also does not have any significant effect on the $Cov(OH^+, OH^+)$ map: the OH^+ (F^+) ions are emitted back-to-back (180°) to each other. The $Cov(H^+, H^+)$ and $Cov(Br^+, H^+)$ maps of 2,5-DHBB show very similar features to the analogous maps of

2,5-DFIB, in which the H^+ ions are ejected at nearly all angles relative to each other. Thus, the 2,5-DHBB and 2,5-DFIB molecules can be distinguished by considering just these five covariance maps, particularly the $Cov(OH^+, H^+)$ and $Cov(F^+, H^+)$ maps, respectively. In the following section, a relatively approximate simulation of the Coulomb explosion of 2,6-DHBB and 2,5-DHBB are investigated in an attempt to characterize fragmentation of the O-H group, and to try to identify the conformers of DHBB present in their respective experimental measurements as a result of the bromine-hydrogen interaction that occurs in the molecule.

5.5.5 Simulation of Experimental Results

Results from a classical many-body Coulomb explosion simulation are presented in this section for 2,6-DHBB and 2,5-DHBB to try to identify the conformers of 2,6-DHBB and 2,5-DHBB that are present in their respective experimental measurements. The simulated DHBB data were generated by Felix Allum and Robert Mason, and the conformer ratio and gas-phase populations of the conformers were calculated by Michael Burt using the B3LYP/LANL2DZ method. Two models were used in the simulations: the single-atom and multi-atom models. In the single-atom model, each atom is treated as a point-charge where Coulombic repulsion occurs between atomic charged fragments (O^+ , Br^+ , H^+ etc.). This is the same model was used to generated the simulated results of DFIB shown in Section 5.3.4.

In the multi-atom model, a certain proportion of molecules can generate multi-atom fragments (*e.g.* OH^+ , CO^+ and C_2^+) as well as atomic fragments (*e.g.* O^+ , H^+ and C^+). In this model, a modification was implemented by Felix Allum which took into account the possibility that some molecules may generate the OH^+ ion, whilst other molecules may generate $O^+ + H^+$ ions following the fragmentation of the OH group. In this modification, a matrix was used to specify the likelihood of combining neighbouring atoms to form two-atom fragment ions.

The influence of forming the two-atom fragment OH^+ on the simulated $Cov(Br^+, H^+)$ covariance maps for 2,5-DHBB molecules is shown in Figure 5.19. In this simulation, the probability of forming C_2^+ (0.38) and CO^+ (0.37) ions was kept constant, with

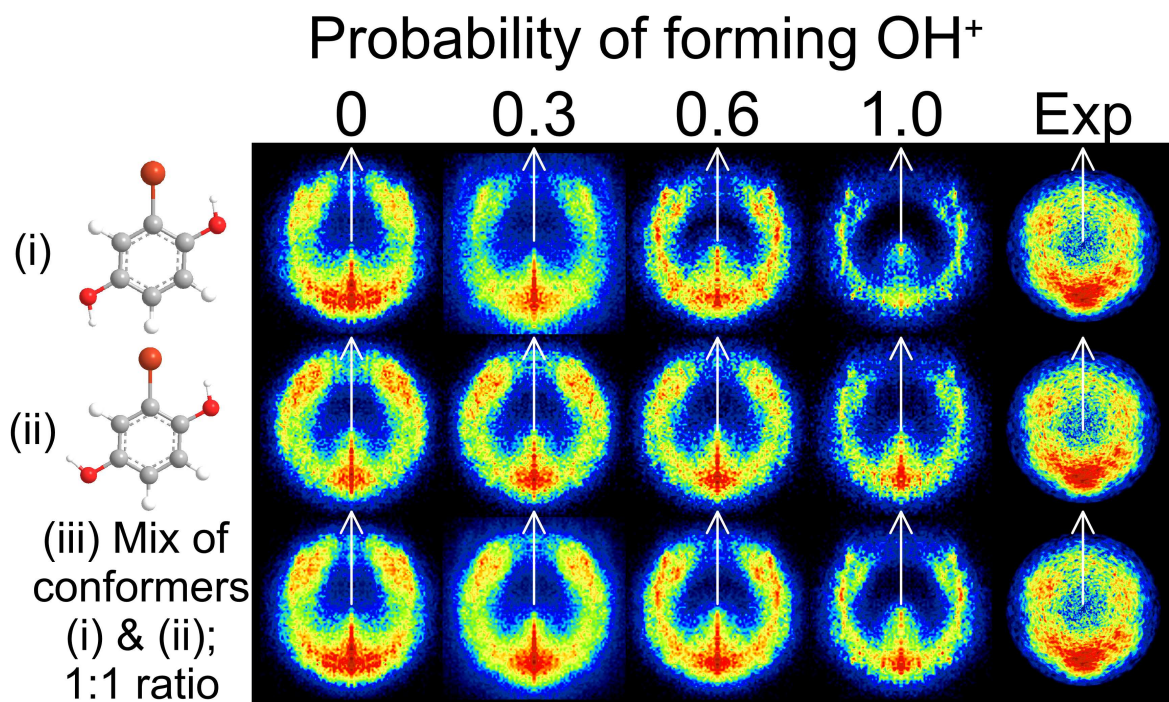


Figure 5.19: Simulated two-fold covariance maps, $Cov(Br^+, H^+)$, are presented for two pure 1D-aligned 2,5-DHBB molecules using the multi-atom model. Each row corresponds to: (i) conformer 1, (ii) conformer 2, (iii) a mixture of the two conformers in a 1:1 ratio. See text in Section 5.5.5 for definition of two conformers. The first four columns of data correspond to the probability of forming OH^+ as a two-atom fragment as opposed to single-atom fragments, O^+ and H^+ . The final column shows the experimental map of $Cov(Br^+, H^+)$ for 1D-aligned 2,5-DHBB molecules. In each map, the reference ion is Br^+ and the plotted ion is H^+ . The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow.

values from Table 5.5. The first two rows in Figure 5.19 correspond to the two most energetically stable conformers of 2,5-DHBB, while the third row is the mixture of these two conformers in a 1:1 ratio (see Section 5.5.5 for further details). The first four columns correspond to different probabilities of forming OH^+ ions which are accompanied by the experimental map (final column). An increase in the likelihood of generating OH^+ ions as opposed to $O^+ + H^+$ ions (column 1 to column 4) leads to a decrease in the covariance between Br^+ and H^+ ions, since fewer H^+ ions are generated. The simulated mixture map at a OH^+ probability of 0.3 qualitatively appears to have the closest match to the experimental map. Thus, in the multi-atom results shown in the rest of this section, the probability of 0.3 for forming OH^+ ions was used.

Simulated results were generated using both models for each conformer as well as for a mixture containing the most energetically stable conformers in their respective

	2,6-DHBB	2,5-DHBB
H ⁺	0.69	0.88
C ⁺	0.25	0.51
C ²⁺	0.00	0.03
OH ⁺	0.52	1.00
Br ⁺	1.00	1.00
Br ²⁺	0.50	0.41
C ₂ ⁺	0.36	0.38
CO ⁺	0.37	0.37

Table 5.5: The integrated signal of the relevant fragments relative to Br⁺ for the two structural isomers of DHBB investigated in this work.

conformer ratios. The goal for the rest of this section is to investigate the feasibility of using the simulated data for the individual conformers of 2,6-DHBB and 2,5-DHBB to definitively identify the conformers that are present in the experimental measurement, results of which are given in the following section.

I. Conformers of 2,6-DHBB

In 2,6-DHBB, there exist three possible conformers. In conformer 1, both hydrogens of the OH group point towards the bromine. The two stabilizing bromine-hydrogen interactions make this the most stable conformer; calculations suggest it forms $\sim 88\%$ of the gas-phase population. The second most stable conformer is the case where the hydrogen of one OH group is pointing towards the bromine and the hydrogen of the other OH group is pointing away. A gas-phase population of $\sim 12\%$ has been predicted for conformer 2 due its the weaker bromine-hydrogen interaction. Whilst in conformer 3, the hydrogen from both OH groups are pointing away from the bromine, and therefore do not possess any stabilizing bromine-hydrogen interactions. Consequently, conformer 3 has been predicted to be too unstable to be observed in the gas-phase. Figure 5.20 shows the two-fold covariance maps for the 2,6-DHBB molecule corresponding to the raw experimental crushed data, the pBasex slice data and simulated crushed data. The corresponding angular distributions for the raw experimental crushed data, the pBasex slice data, and the simulated crushed data for a mixture containing conformers 1 and 2 in a 88:12 ratio are shown in Figure A.10 in Appendix A.

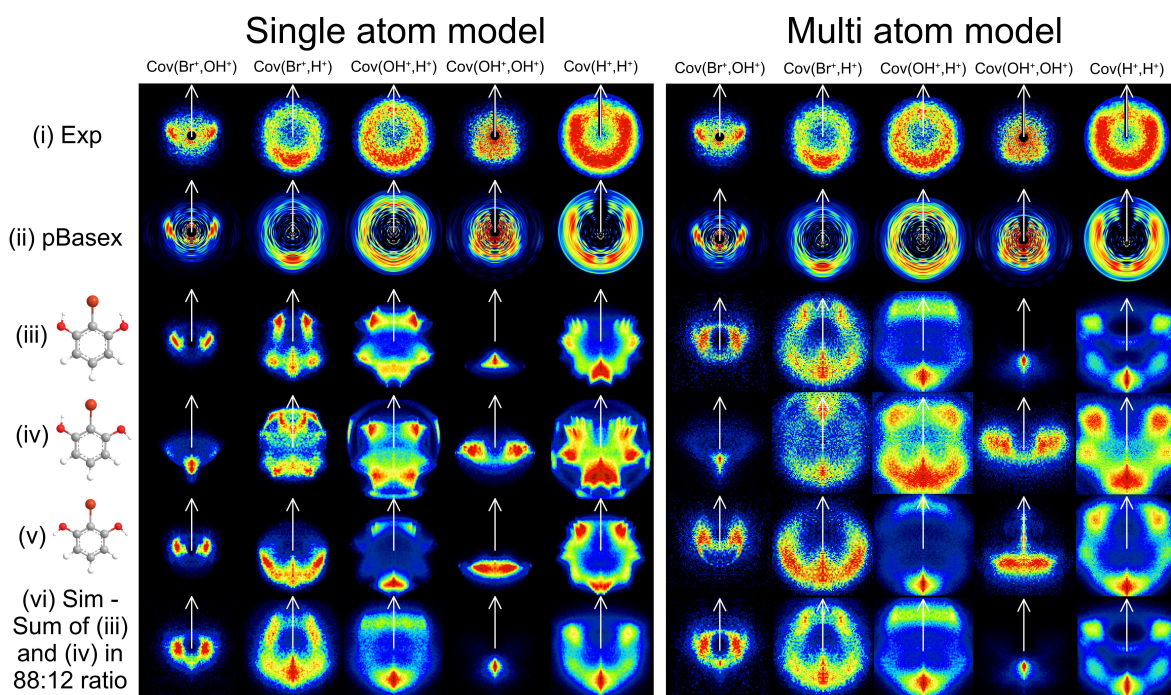


Figure 5.20: Two-fold covariance maps, $Cov(X, Y)$, of 1D-aligned 2,6-DHBB. Each row corresponds to: (i) experimental data, (ii) their corresponding pBasex-inversion, simulated data for (iii) conformer 1, (iv) conformer 2, (v) conformer 3, and (vi) the sum of conformers 1 and 2 in a 88:12 ratio. Simulated results are shown for both the single atom (left) and multi atom (right) models. Each column presents a two-fold covariance map, $Cov(X, Y)$, with the reference ion denoted as X and the plotted ion denoted as Y . The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow. Simulated results were generated by Felix Allum under my supervision. The conformer ratio was determined by Michael Burt through DFT calculations using the B3LYP/LANL2DZ method.

No one conformer from either model gives a perfect agreement with all experimental maps. However, conformer 1 from the single-atom model does have an excellent agreement with the $Cov(Br^+, OH^+)$ experimental map. In this case, treating the OH^+ ion as a single particle in the single-atom simulation with m/q of 17 provides much better agreement than in the multi-atom case, where in the latter case OH^+ ions were generated in 30% of molecules while $O^+ + H^+$ ions were generated in 70% of molecules.

In $Cov(Br^+, H^+)$, conformer 1 from the multi-atom model instead gives the best agreement with experimental data. Conformer 2 from the same model best reproduces the features in the $Cov(OH^+, H^+)$ map. This shows that the hydrogen in the OH group clearly contributes towards these two maps of 2,6-DHBB. While the broad feature in the $Cov(OH^+, OH^+)$ experimental map could not be reproduced by any of the three conformers using both models.

In summary, although some features can be reproduced better by one model than in the other, both models cannot definitively reproduce all features in the experimental maps. Consequently, the conformers of 2,6-DHBB that exist in the experimental measurement cannot be definitively identified using these models alone.

II. Conformers of 2,5-DHBB

In 2,5-DHBB, there exist four possible conformers. In conformers 1 and 2, the hydrogen from one OH group ($\sim 60^\circ$ to bromine) is pointing towards the bromine atom. These two conformers are differentiated by the hydrogen on the second OH group ($\sim 240^\circ$ to bromine) pointing towards or away from the bromine atom, respectively. The gas-phase population of 2,5-DHBB is predicted to be composed of only these two conformers in equal proportion, since conformers 3 and 4 have been predicted to be too unstable to be observed in the gas-phase measurements (since the hydrogen on the closest OH group to the bromine atom is pointing away from it).

Figure 5.21 shows the experimental, pBasex-inverted and simulated two-fold covariance maps for the 2,5-DHBB molecule. The corresponding angular distributions of the raw experimental data, the pBasex data, and the simulated data for a mixture containing conformers 1 and 2 in a 1:1 ratio is shown in Figure A.11 in Appendix A. No one conformer shows a perfect agreement with the experimental data from either model, although the simulated data for conformers 1 and 2 have the closest match to the experimental data.

The summed simulated covariance maps for the mixture containing conformers 1 and 2 in a 1:1 ratio (last row of Figure 5.21), using the single-atom model, do show similar features to the experimental data. In the $Cov(Br^+, OH^+)$ map, the single-atom model best reproduces the four-fold feature that is present in the experimental data. While the multi-atom model performs better at reproducing the “horseshoe” feature in the $Cov(Br^+, H^+)$ map. Similar results are generated by both models in the $Cov(OH^+, OH^+)$ and $Cov(H^+, H^+)$ simulated maps, which agree to a certain extent with the experimental data. In the $Cov(OH^+, H^+)$ map, some discrepancies exist between both simulated models and the experimental data, such as the appearance of

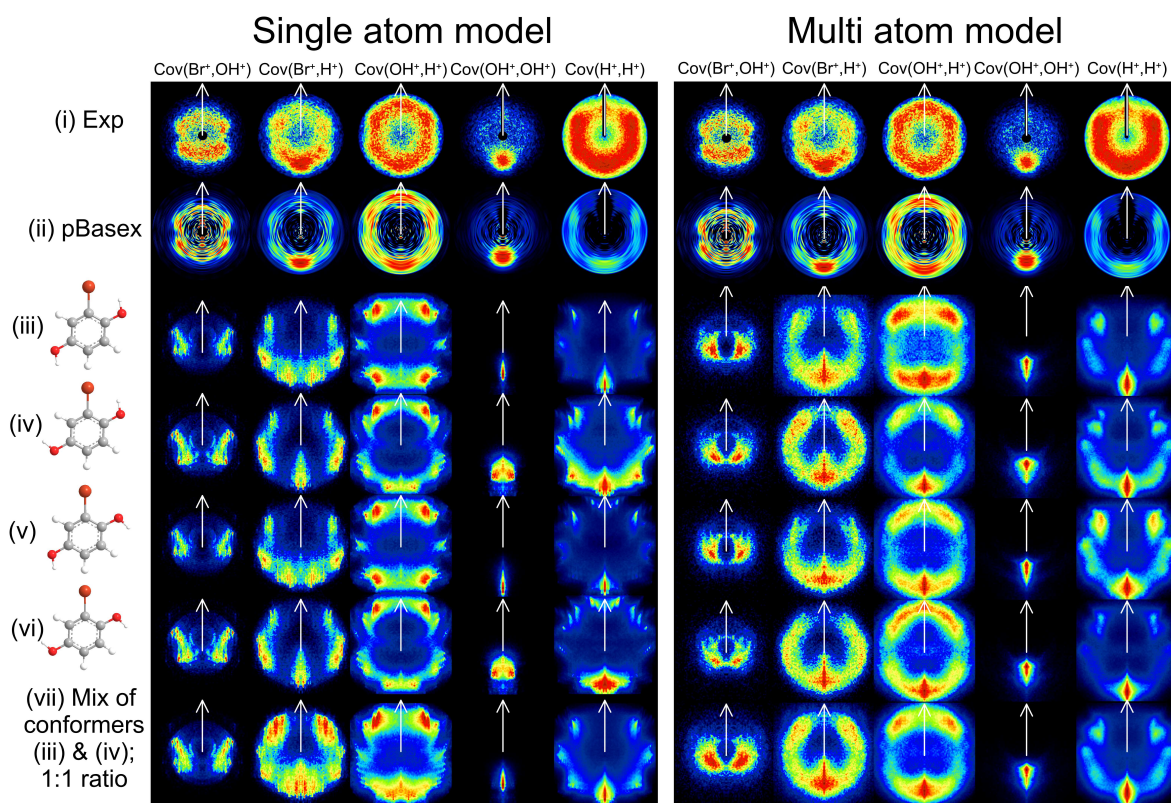


Figure 5.21: Similar to Figure 5.20 but for 1D-aligned 2,5-DHBB. Each row corresponds to (i) the raw experimental data, (ii) their corresponding pBasex-inversion, simulated data for (iii) conformer 1, (iv) conformer 2, (v) conformer 3, (vi) conformer 4, and (vii) the sum of conformers 1 and 2 in a 1:1 ratio. Simulated results are shown for both the single atom (left) and multi atom (right) models. Each column presents a two-fold covariance map, $Cov(X,Y)$, with the reference ion denoted as X and the plotted ion denoted as Y . The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow. Simulated results were generated by Robert Mason under my supervision. The conformer ratio was determined by Michael Burt through DFT calculations using the B3LYP/LANL2DZ method.

only three or four recoil angles in the simulated angular distributions, while six recoil angles are observed in the experimental data.

In general, the simulations cannot definitively identify each conformer that may be present in the experimental data. This may be due to the simulation not accounting for one or more issues in the Coulomb explosion of DHBB, or that the CEI technique may not have the scope to experimentally identify the conformers of 2,6-DHBB and 2,5-DHBB. The following section compares unaligned data to the 1D-aligned data, with the latter already shown to give a rich array of structural information on the parent molecules in both pure and mixed samples of DFIB and DHBB. The comparison will determine whether similar quality covariance maps can be obtained in the absence of

the adiabatic alignment pulse.

5.6 The Effect of the Alignment Pulse

In this section, the influence of the alignment laser on the fragmentation of the molecule and subsequent correlations between ions is investigated through a comparison of unaligned and 1D-aligned DFIB data. The ToF spectra recorded by the PImMS2 camera for unaligned (solid traces) and 1D-aligned (dashed traces) are shown in Figure 5.22 for 2,5-DFIB (top row, green trace), 3,5-DFIB (middle row, red trace) and 2,6-DFIB (bottom row, black trace). In all three molecules, the alignment laser clearly breaks down the large molecular fragments, such as the molecular ion, to generate a ToF spectra that is dominated by atomic and small molecular fragments.

The two-fold covariance maps of unaligned and 1D-aligned 3,5-DFIB molecules are shown in Figure A.6(a) and (b) in Appendix A. Although several of the unaligned two-fold covariance maps are less well-resolved than in the 1D-aligned data, the two sets of data in general are remarkably similar. The most significant maps for both sets of data are shown in Figure 5.23. Here, the unaligned maps in panel (a) were normalised to the maximum intensity of their corresponding 1D-aligned data shown in panel (b) to aid in comparison, with several interesting differences and similarities. The unaligned experimental covariance maps (top row) contain significantly weaker covariances between the two ions of interest than in the 1D-aligned case.

The corresponding simulated data (third row) shows the same trend, where a weaker two-fold covariance is visible in the unaligned simulated data. Interestingly, the pBasex slice images (second row) look very similar in both cases, suggesting that the unaligned two-fold covariance maps contain sufficient statistics to generate well-resolved pBasex slice images. The corresponding simulated slice data (bottom row) also shows a good qualitative agreement and comparable intensities between the unaligned and 1D-aligned cases.

The angular distributions from these two-fold covariance maps are shown in Figure 5.24. Panel (a) shows the distributions from the experimental maps (top row, Figure

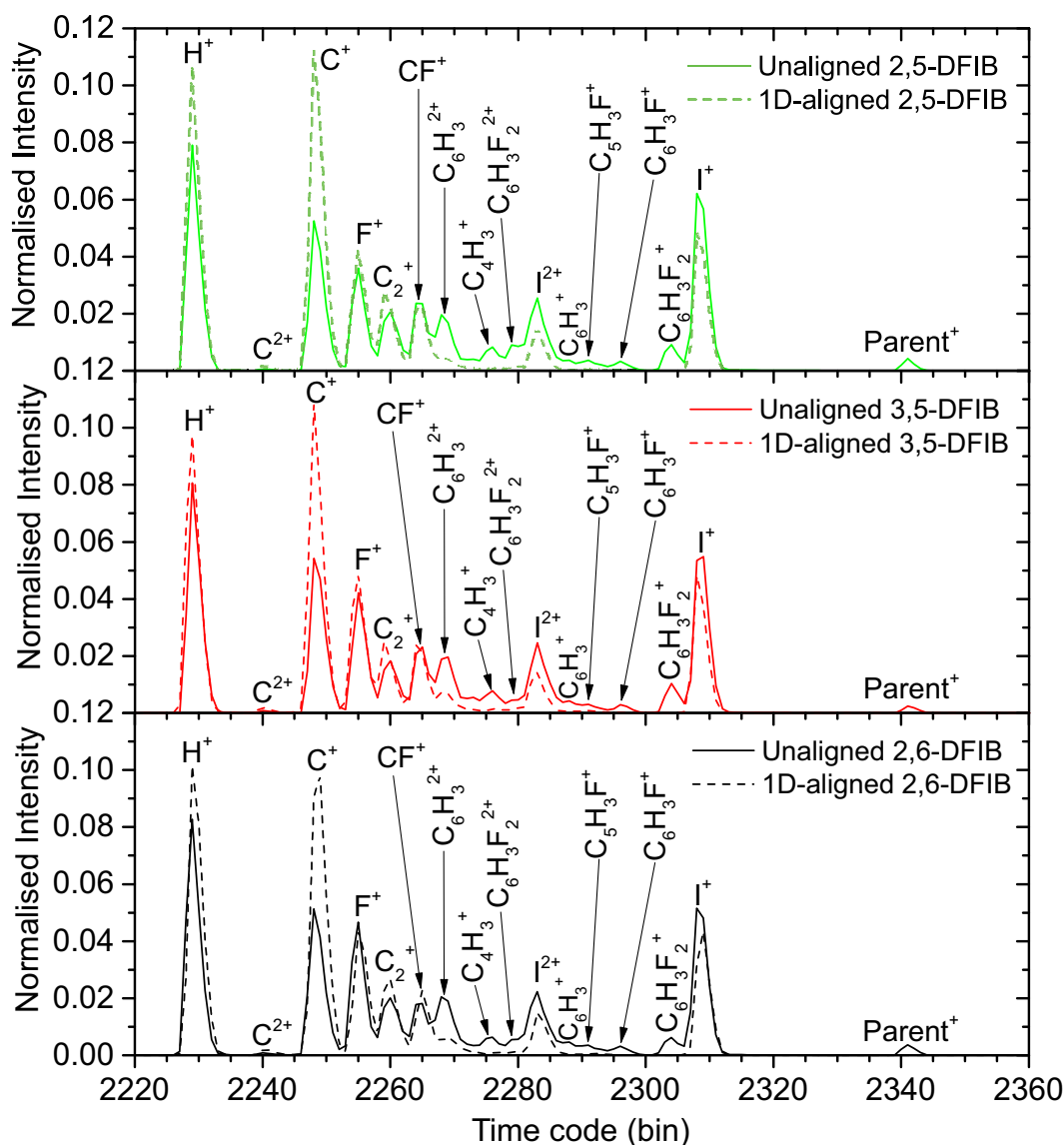


Figure 5.22: Time-of-flight spectra recorded by the PImMS2 camera for unaligned (dash trace) and 1D-aligned (solid trace) DFIB molecules following strong-field ionization with an intense 800 nm pulse polarized parallel to the detector plane. Measurements for 2,5- (top row, green trace), 3,5- (middle row, red trace), and 2,6- (bottom row, black trace) pure isomers of DFIB are shown. Each ToF distribution was normalised by its corresponding total ion count.

A.6) for the unaligned (black solid trace) and aligned (red dashed trace) cases. In general, the 1D-aligned data show approximately 50% stronger two-fold covariances than the unaligned data. The corresponding simulated data are shown in panel (c) and were generated using the ToF information gathered from the experimental measurements. The simulation takes into account the alignment pulse's ability to break down large molecular fragments into atomic and small molecular fragments.

The $Cov(I^+, F^+)$ map shows an excellent match between the experimental and

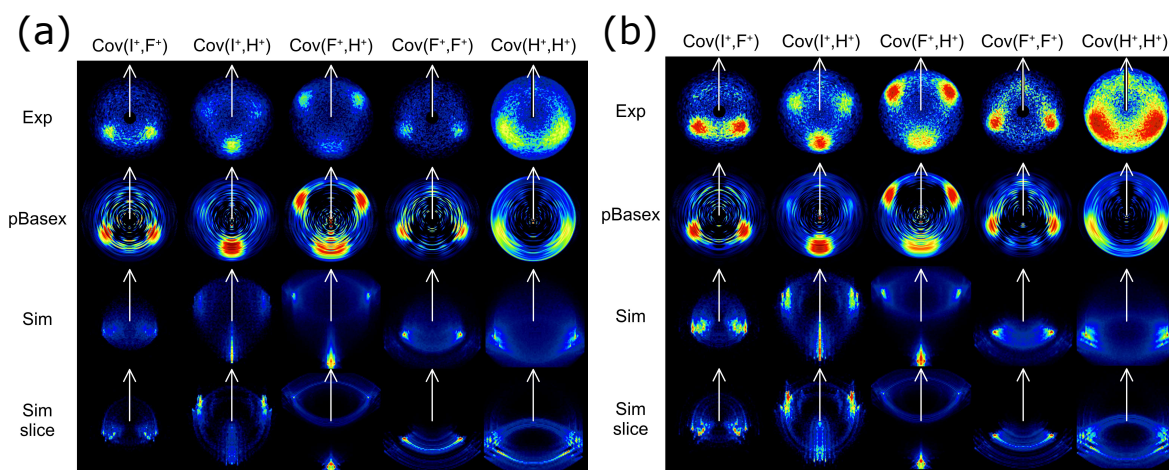


Figure 5.23: Two-fold covariance maps, $Cov(X, Y)$, are presented for (a) unaligned and (b) 1D-aligned 3,5-DFIB molecules. The four rows correspond to the experimental crushed data (top row), pBasex-inverted data (second row), the simulated crushed data (third row), and the simulated slice data (bottom row). Each column presents a two-fold covariance map, $Cov(X, Y)$, with the reference ion denoted as X and the plotted ion denoted as Y . The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow. The maps in panel (a) were normalised to the maximum intensity of the corresponding map in panel (b).

simulated data, and it shows that the alignment of molecules is crucial in detecting stronger correlations between the I^+ and F^+ ions. Although the agreement between the experimental and simulated data is not as good in the subsequent four maps, the 1D-aligned experimental data do generate stronger correlations between the pair of ions in all of these maps when compared to the unaligned experimental data for the same number of laser shots. Thus, the alignment of molecules does increase the correlations seen in these four pairs of ions.

Interestingly, the pBasex slice distributions in panel (b) for the two cases are nearly identical; a similar agreement is also observed in the corresponding simulated data in panel (d). This is explained by the fact that the molecules in the slice data are all in the plane of the detector, making it easier to detect the correlations between fragment ions. The rationale behind this is that the correlations in the covariance maps are between two or three ions of all pixels in the PImMS sensor, which corresponds to the plane of the MCPs that the ions impact on.

Two-fold covariance maps are presented for unaligned 2,6-DFIB and 2,5-DFIB

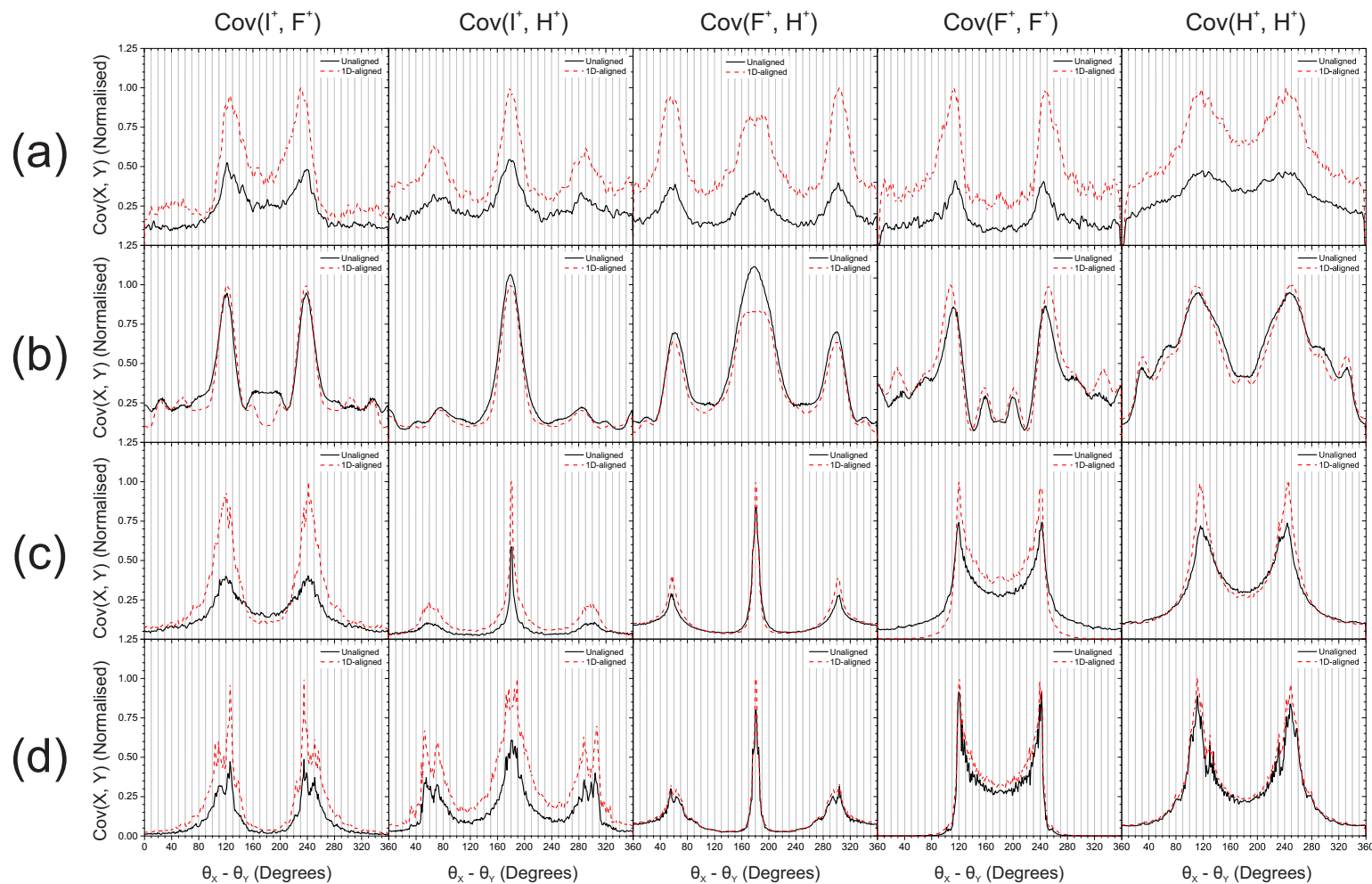


Figure 5.24: Comparison between unaligned (black trace) and 1D-aligned (red dashed trace) through the angular distributions of the two-fold covariance maps shown in Figure 5.23 for (a) the raw experimental crushed data, (b) the pBasex slice data, (c) the simulated crushed data and (d) the simulated slice data. The angular distributions for the unaligned data were normalised to the maximum intensity of the corresponding 1D-aligned distribution to aid in comparisons.

molecules in Figure A.7 in Appendix A. It should be noted that the data presented in this figure were recorded for approximately 16,000 laser shots, which is approximately one third of the statistics recorded for the corresponding 1D-aligned data. This explains the lower signal:noise present in the unaligned maps.

The two-fold covariance maps for 1D-aligned and unaligned data are shown for 2,6-DHBB in Figure A.8 and for 2,5-DHBB in Figure A.9, both in Appendix A. In the 2,6-DHBB case, the $Cov(Br^+, OH^+)$ maps appear equally well-resolved with and without the alignment laser (stronger correlation was observed in the $Cov(I^+, F^+)$ map of 3,5-DFIB molecules with the alignment pulse). The features in the $Cov(H^+, H^+)$ maps of both 2,6-DHBB and 2,5-DHBB molecule are equally well-resolved also with and without the alignment pulse, however a significant improvement in the correlation of H^+ ions was observed with the alignment pulse for 3,5-DFIB. Both the $Cov(OH^+, H^+)$ and $Cov(OH^+, OH^+)$ maps are less well-resolved in the absence of the alignment pulse (in both DHBB molecules), which was also the case for 3,5-DFIB.

The recoil angles from both 1D-aligned and unaligned cases are in general identical, and the main difference between the two cases are in the intensities of their covariance maps, where a stronger correlation exists between ions in the 1D-aligned data than in the unaligned data.

5.7 Summary

In summary, four structural isomers of DFIB and two structural isomers of DHBB were successfully Coulomb exploded using an intense 800 nm pulse, with the resulting fragment ions recorded by the PImMS2 camera. The ion images for the different isomers showed similar features and were insufficient to identify the structural isomers in each measurement. Two- and three-fold covariance maps were used to reveal unique correlations between two or three fragment ions of an isomer. The experimental two-fold covariance maps were used to identify the four structural isomers of DFIB and two structural isomers of DHBB. A four-fold feature was present in the $Cov(I^+, F^+)/Cov(Br^+, OH^+)$ experimental two-fold maps of 2,5-DFIB/2,5-DHBB, re-

spectively. This four-fold feature in fact corresponded to two particular geometries of 2,5-DFIB, as confirmed by the $Cov(I^+, F^+, F^+)/Cov(Br^+, OH^+, OH^+)$ experimental three-fold covariance maps, respectively. In addition, a measurement containing a mixture of 3,5- and 2,4-DFIB was investigated. The identity and abundance ratio of the two structural isomers were determined by comparing the covariance experimental maps of the corresponding pure structural isomers to the mixture data, in which it was determined that the mixture contained 3,5-DFIB and 2,4-DFIB in a 2:1 ratio.

In DHBB, the OH^+ and Br^+ fragments are analogous to the F^+ and I^+ fragments in DFIB. Strong correlations between both OH^+ and Br^+ fragments were recorded for both DHBB isomers in the experimental covariance maps. The H^+ ions were emitted at additional recoil angles when compared to DFIB since the 800 nm probe pulse was able to fragment the O-H group. These additional recoil angles from the experimental data were subsequently used to distinguish 2,5-DHBB and 2,6-DHBB from 2,5-DFIB and 2,6-DFIB. The results of DHBB presented in this chapter open up the possibility for future CEI experiments to be carried out on biologically relevant molecules, such as carbohydrates and amino acids. Simulated data were also generated for both DFIB and DHBB molecules. In DFIB, the simulated data showed a very good agreement with the experimental data. While in DHBB, the simulated data could not reproduce all the significant features in the experimental data. Thus, it was not possible to identify the conformers of DHBB that were present in the experimental measurement.

The effect of the adiabatic alignment pulse was also investigated. It was shown that the unaligned and 1D-aligned data were remarkably similar. This is of particular interest since the adiabatic alignment pulse cannot be used in time-resolved pump-probe measurements as it may influence the electronic structure of the molecule. In the following chapter, the CEI technique coupled with covariance analysis is extended to femtosecond-resolved pump-probe measurements on the *trans-cis* isomerization in unaligned 4,4'-difluoroazobene.

Chapter 6

Time-Resolved *Trans-Cis*

Isomerization of

4,4'-difluoroazobenzene

6.1 Introduction

Azobenzene (AB) exists in either the *trans* or *cis* geometry due to restricted rotation about the N=N double bond. Extensive studies have been carried out into the *trans-cis* and *cis-trans* photoisomerization of azobenzene and its derivatives through optical schemes, with an extensive review presented in Ref. [293]. Figure 6.1(a) shows the Jablonski diagram for the $S_2 \leftarrow S_0$ excitation and subsequent relaxation pathways in *trans*-AB [293].

Four distinct time constants, corresponding to four different decay steps, have been previously identified from the decay of excited *trans*-AB molecules following the $S_2 \leftarrow S_0$ excitation [293]: 110 - 200 fs, $\sim$ 400 fs, 500 - 1000 fs, and 10 - 100 ps [293]. The shortest lifetime corresponds to the $S_1 \leftarrow S_2$ internal conversion [293–296]. This is then followed by departure from the Frank-Condon region in the S_1 state which takes approximately 400 fs [293, 297].

Internal conversion to the S_0 state takes approximately 500 - 1000 fs and is accom-

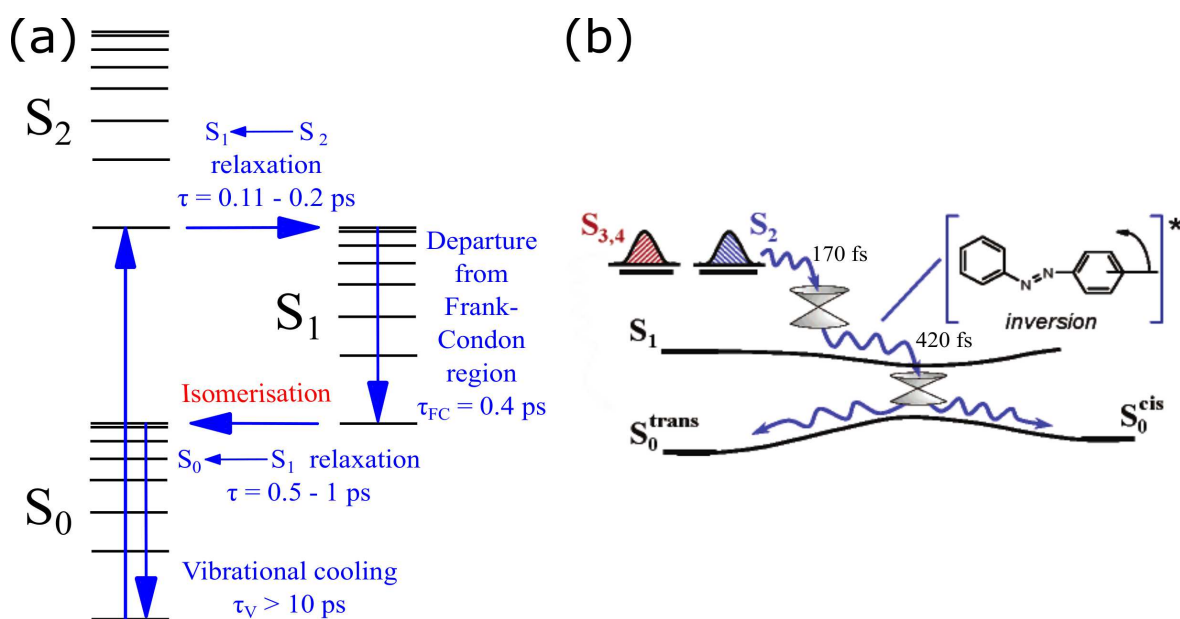


Figure 6.1: (a) The $S_2 \leftarrow S_0$ excitation and subsequent relaxation scheme in *trans*-azobenzene is shown using a simplified Jablonski diagram. The $S_2 \leftarrow S_0$ excitation is followed by rapid internal conversion into the S_1 state. Departure from the Frank-Condon region in the S_1 state is quickly followed by $S_0 \leftarrow S_1$ internal conversion and subsequent isomerization of *trans*-azobenzene. In the S_0 state, the molecule is vibrationally cooled. This panel was adapted from Ref. [293]. (b) Schematic showing the possible isomerization that may occur as the excited *trans*-azobenzene molecule relaxes back down to its ground electronic state, S_0 , into either the *trans* or *cis* isomer. This panel was adapted from Ref. [294].

panied by isomerization of the *trans*-azobenzene molecule [293, 295, 296, 298]. Subsequent vibrational cooling of the molecule occurs on the tens of picosecond timescale. Figure 6.1(b) shows the isomerization pathways for the $S_0 \leftarrow S_1$ internal conversion. The excited *trans*-azobenzene molecule relaxes to its ground electronic state, S_0 , or it isomerizes to the *cis* isomer [293, 294]. The quantum yield for isomerization of azobenzene in the S_1 state has been reported to be 25% by Stolow and coworkers [294]. Early theoretical calculations predicted that isomerization of *trans*-azobenzene proceeds via a concerted inversion [299, 300]. By contrast, dynamical studies later predicted that isomerization occurs by inversion-assisted rotation [301–303]. Stolow and coworkers also identified two time constants of 170 fs and 420 fs [294] following the 330 nm pump and subsequent 207 nm probe of *trans*-azobenzene molecules in a gas-phase time-resolved photoelectron spectroscopy study. They assigned the short time constant to the $S_1 \leftarrow S_2$ internal conversion, which is in good agreement with previous work [293, 295, 296, 298]. Although Stolow and coworkers assigned the long time

constant to the lifetime of $S_{3,4}$ states, theoretical calculations by Ciminelli *et al.* later found the S_3 excited state lifetime to be ~ 100 fs. Thus, it is thought to be unlikely that the $S_{3,4}$ states can live for a longer duration than the S_2 state [293, 302, 304]. Instead, Ciminelli *et al.* [302] reassigned the time constant of 420 fs in the work of Stolow and coworkers as the S_1 lifetime, which is in agreement with other experimental studies [293, 295, 296]. It should also be noted that no experimental results were presented by Stolow and coworkers that showed *trans-cis* photoisomerization had occurred in azobenzene.

In the work presented in this chapter, jet-cooled (E)-4,4'-difluoroazobenzene (DFAB) molecules are irradiated by a 330 nm pump pulse and subsequently Coulomb exploded with an intense 35 fs 800 nm pulse. The fluorinated derivative of the azobenzene molecule was studied in order to obtain two-fold covariances between the two fluorines, analogous to the studies (of the four isomers of difluoriodobenzene) presented in Chapter 5. Knie *et al.* reported that placing electron-withdrawing groups (EWGs), such as fluorine, at the ortho position in the azobenzene molecule leads to the separation of the $n \rightarrow \pi^*$ bands of both the *cis* and *trans* isomers [305]. Placing additional EWGs at the para position as well as the ortho position leads to a further enhancement of this separation [305]. No literature has been reported on the dynamics or the electronic structure of (E)-4,4'-difluoroazobenzene molecules, and it is assumed to be approximately similar to the electronic structure of bare azobenzene; *i.e.* fluorinating azobenzene at the para position is assumed to not significantly alter the electronic structure of the molecule.

In this chapter, the two-fold covariance technique, discussed in detail in Chapter 5, is extended to the time-resolved study of *trans-cis* isomerization of 4,4'-difluoroazobenzene (DFAB) using CEI coupled with the PImMS1 camera. The angular correlations between the recoil ions are investigated to monitor changes in the structure of DFAB following *trans-cis* isomerization.

6.2 Experimental Methods

The results presented in this chapter were generated with the Aarhus VMI spectrometer at a repetition rate of ~ 200 Hz. (see Chapter 2 for detailed description). A brief overview of the experimental set-up and parameters are given in this section. A sample of *trans*-4,4'-difluoroazobenzene, which is a liquid at room temperature, was placed inside the inlet compartment of the Even-Lavie valve and was heated to 70° to generate a gaseous sample. The gaseous target molecule was seeded in He (total gas mixture pressure of 80 bar) and expanded through the nozzle of the pulsed Even-Lavie valve.

The resulting molecular beam was intersected by two femtosecond pulses: a 330 nm pump pulse and an 800 nm probe pulse. The 330 nm pump pulse had a pulse duration of ~ 115 fs (FWHM), a beam width of $31\ \mu\text{m} \times 68\ \mu\text{m}$, and a pulse energy of $1.6\ \mu\text{J}$. The intensity of the pump pulse ($3.3 \times 10^{11}\ \text{Wcm}^{-2}$) was weak to avoid strong-field ionization of molecules. The polarization was linear and controlled by a HWP. The 800 nm probe pulse had a pulse duration of 35 fs (FWHM), a beam width of $20\ \mu\text{m} \times 20\ \mu\text{m}$, and a pulse energy of $67\ \mu\text{J}$. This generated peak intensities of up to $2 \times 10^{14}\ \text{Wcm}^{-2}$. The cross correlation between the pump and probe pulses was 120 fs (FWHM). The time delay between the two pulses were adjusted by shortening or lengthening the distance that the probe pulse had to travel using a computer-controlled delay stage (Micos, LS-110).

The Aarhus spectrometer was operated in crushed imaging VMI mode, and the following $V_R : V_E : V_G$ ratio of 1.000:0.660:0.000 was used. In the parallel geometry, an absolute voltage of 6000 V was applied to the repeller electrostatic plate, while a voltage of 4500 V was used in the perpendicular geometry. The ion imaging detector was operated with a voltage difference of around 1800 V applied across the MCPs, and a voltage difference of 3000 V applied between the back face of the back MCP and the phosphor screen. The PImMS1 camera captured the flashes of light that were emitted from the back of the P47 phosphor screen.

6.3 Experimental Results

The ion yield, ion images, and subsequent two-fold covariance analysis are investigated to explore the *trans-cis* photoisomerization of DFAB molecules at 330 nm.

6.3.1 Excited Electronic State Dynamics

In this section, the excited electronic state dynamics of (E)-4,4'-difluoroazobenzene (DFAB) are investigated and compared to literature. The time-of-flight spectra recorded with the PImMS1 camera are shown in Figure 6.2 for unaligned *trans*-DFAB molecules probed with an 800 nm pulse polarized either parallel (top trace) or perpendicular (bottom trace) to the detector plane. It should be noted that the spectrometer voltages used in the parallel configuration were 1.5 times higher than in the perpendicular configuration, and hence leads to the expanded ToF spectrum in the latter configuration relative to the former. There is a significant contribution from large molecular fragments in both ToF traces, as has been previously observed in unaligned DFIB and DHBB molecules. The F^+ ToF profile in the perpendicular configuration has two components which correspond to the detection of fluorine fragments that were facing towards (away from) the detector as illustrated by the sketch in the perpendicular ToF panel. This leads to the early (late) component of the ToF profile marked F_f^+ (F_b^+). While in the parallel configuration, the F^+ ToF profile has only one component as both fluorine fragments in the molecule are equally separated from the detector, as shown by the sketch in the panel, and therefore have approximately the same arrival-time.

The ion images recorded simultaneously by the PImMS1 camera are shown above the ToF traces for the most significant fragments. In the perpendicular case, the images are all isotropic since the molecule was not aligned in space and was free to rotate around the axis perpendicular to the detector (*i.e.* the ToF axis). In the parallel case, the F^+ , $C_6H_4^+$, and $C_6H_4F^+$ fragments contain anisotropic distributions as a result of geometric alignment effects. As seen in Chapter 7, this is due to the enhanced ionization probability for molecules with their most-polarizable axis (MPA), which is along the F-F coordinate in DFAB, parallel to the polarization axis of the probe pulse.

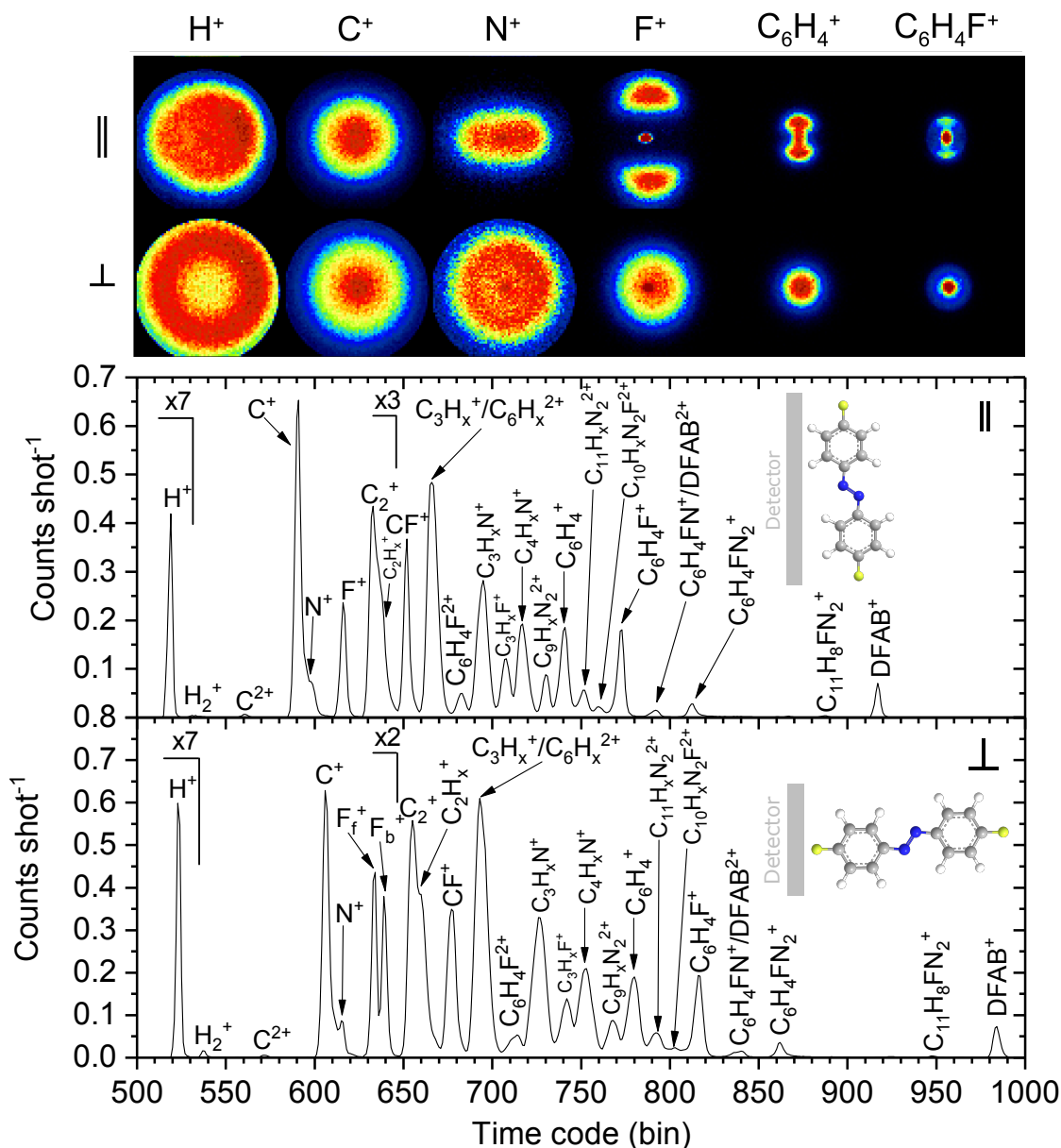


Figure 6.2: Time-of-flight spectra recorded by the PImMS1 camera for 4,4'-difluoroazobenzene (DFAB) molecules following photoexcitation by a 330 nm pulse and strong-field ionization with an intense 800 nm pulse. Both pulses were polarized either parallel (top trace) or perpendicular (bottom trace) to the detector plane. The corresponding laboratory-frame ion images are shown above the ToF traces for the most significant ion fragments. Each ToF distribution was normalised to its corresponding total number of laser shots.

Thus, geometric alignment was used in this work to selectively ionize molecules with a particular spatial distribution in order to improve correlations between ions.

Geometric alignment as opposed to adiabatic laser alignment was used in this work as the latter would impart energy into the molecule and alter the electronic structure of the molecule. Non-adiabatic laser alignment pulses were not available in the experimental set-up at the time of this work. A $\langle \cos^2 \theta_{2D} \rangle$ value of 0.85 was extracted from

the F^+ ion images in the parallel configuration. The corresponding $\langle \cos^2 \theta_{2D} \rangle$ values for phenyl ($C_6H_4^+$) and phenylfluorine ($C_6H_4F^+$) fragments were 0.72 and 0.69, respectively. Interestingly, the N^+ ions are ejected perpendicular (but in the same plane) to the polarization vector of the 800 nm pulse, giving a $\langle \cos^2 \theta_{2D} \rangle$ value of 0.40 and a β parameter of -0.89. Thus, the N^+ ions are ejected perpendicular to the F^+ , $C_6H_4^+$, and $C_6H_4F^+$ ions in the DFAB molecule.

Maps of time-of-flight as a function of pump-probe delay are shown in Figure A.12 in Appendix A.2 for parallel and perpendicular configurations in panels (a) and (b), respectively. In both configurations, there is a large increase in signal for all ToFs at very early pump-probe delays, accompanied by an exponential decay in yield with increasing delay. The total ion yield as a function of delay is shown in Figure 6.3 for both configurations. In the parallel case shown in panel (a), single and bi-exponential fits were applied to the experimental data, with the better agreement achieved with the latter. In the perpendicular data shown in panel (b), only a single exponential fit could be applied to the data.

The lifetimes extracted from these total ion yields are presented in Table 6.1. The short lifetime (~ 600 fs) that is common to all three possible exponential fits falls between 500 - 1000 fs, which has been assigned as the $S_0 \leftarrow S_1$ relaxation pathway by Bandara and Burdette [293]. In the gas-phase work on azobenzene by Stolow and

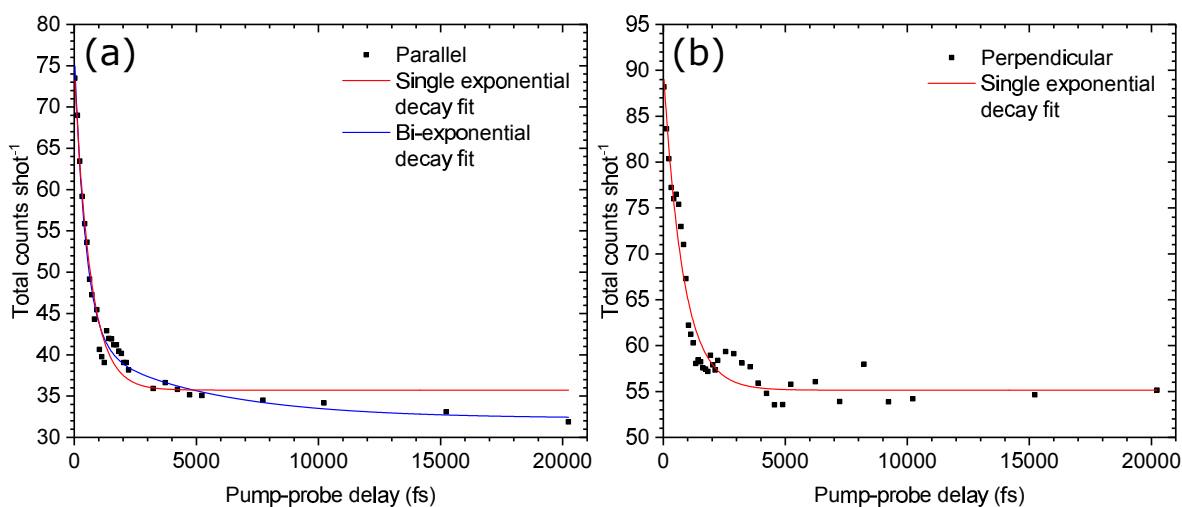


Figure 6.3: The total ion yield as a function of pump-probe delay for both (a) parallel and (b) perpendicular configurations. In panel (a), a single (red) and a bi-exponential (blue) decay fits are shown, while in panel (b) only a single exponential could be applied.

	Single exponential	Bi-exponential
Parallel	649 ± 47	463 ± 52 and 4937 ± 2676
Perpendicular	796 ± 63	-

Table 6.1: Table of lifetimes extracted from single and bi-exponential decay fits to the total ion yield plots as shown in Figure 6.3 for both parallel and perpendicular configurations. Values are given in femtoseconds.

cowokers at 330 nm, they also observed a lifetime of 420 fs which was reassigned as the S_1 lifetime by Bandara and Burdette [293]. The long lifetime (~ 5000 fs) that is only observed in the bi-exponential fit to the parallel data may correspond to the vibrational cooling of the S_0 state [293]. It should be noted that the assignment for the long lifetime should be taken with caution as the associated fitting error is approximately 50% of the extracted lifetime (~ 2500 fs), and also the large time constant only appears in the parallel data. After relaxation to S_1 following $S_2 \leftarrow S_0$ excitation, *trans-cis* isomerization occurs during $S_0 \leftarrow S_1$ internal conversion and not directly from the S_2 state [293].

Figure 6.4 shows sketches of *trans*-DFAB (left column) and *cis*-DFAB (right column) positioned either parallel (top row) or perpendicular (bottom row) to the plane of detector. In *trans*-DFAB, the two fluorines are positioned at roughly 180° to each other in the molecule. Thus, the fluorines are expected to fly in the opposite direction to each other (*i.e.* back-to-back emission) during the Coulomb explosion of *trans*-DFAB molecules, as shown in Figure 6.4(a). While in *cis*-DFAB molecules, the two fluorines are approximately 120° to each other in the molecule. Consequently, the fluorines are expected to fly at a much smaller angle to each other when compared to *trans*-DFAB, as shown in Figure 6.4(b). In the perpendicular geometry, the fluorines in *trans*-DFAB will be detected at roughly the same position on the detector, as shown in Figure 6.4(c). While in *cis*-DFAB, the fluorines be detected at two separate positions that are separated by a relatively large distance, as shown in Figure 6.4(d).

In the probe-only measurements, only ground-state *trans*-DFAB molecules are present since a jet-cooled molecular beam of *trans*-DFAB molecules was pumped and probed by the 330 nm and 800 nm pulses, respectively. While in the pump-probe mea-

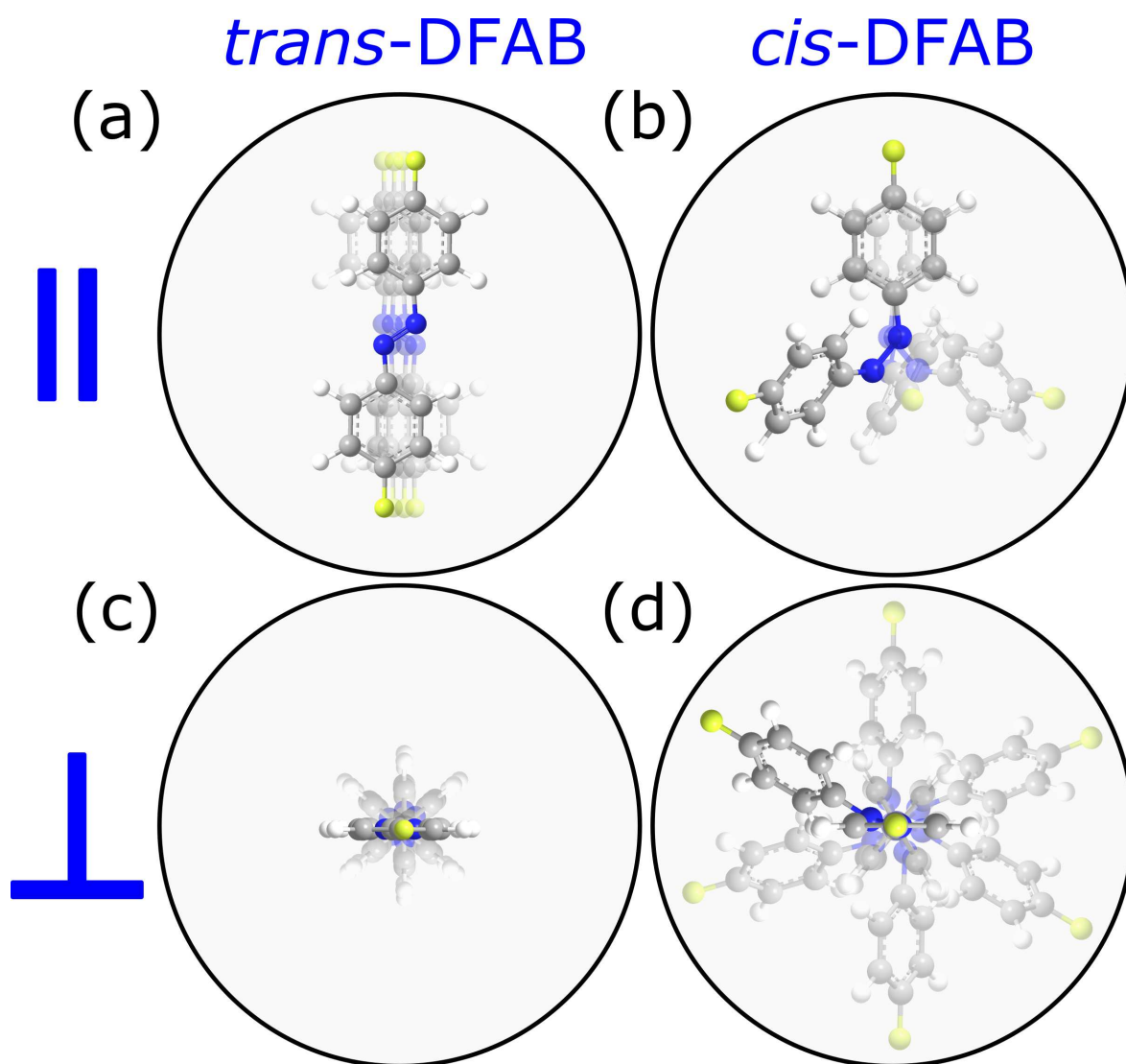


Figure 6.4: Sketches of *trans*-DFAB (left column) and *cis*-DFAB (right column) positioned either parallel (top row) or perpendicular (bottom row) to the plane of the detector.

surements, only a small proportion ($\sim 20\%$) of ground-state *trans*-DFAB molecules will have been excited by the 330 nm pulse. Thus, the pump-probe data will have a large contribution ($\sim 80\%$) from *trans*-DFAB molecules in their ground-state, and therefore a mixture of both isomers will appear at relatively large pump-probe delays in the pump-probe data. Therefore, it is possible to monitor whether *trans-cis* isomerization has been successfully achieved by monitoring the F^+-F^+ emission angles using $Cov(F^+, F^+)$ two-fold covariance maps from probe-only and pump-probe data, as discussed further in the next section.

6.3.2 Time-Resolved Two-Fold Covariances

The two-fold covariance maps, $Cov(F^+, F^+)$, for the parallel and perpendicular configurations are shown in Figures 6.5 and 6.6, respectively. In each figure, the time-resolved and the probe-only covariance maps are presented, along with a sketch of the molecule's position relative to the detector plane. In each map, one of the F^+ ions is set as the reference ion and is confined to the vertical vector indicated by the white arrow in each map. The second F^+ ion is plotted in covariance to the reference ion (*i.e.* $Cov(F^+, F^+)$) at each pixel in the map. In both figures, all pump-probe maps have been normalised to the maximum intensity of the corresponding probe-only map.

In the parallel configuration, the probe-only map has a local maximum at around 180° which corresponds to the back-to-back emission of F^+ ions in *trans*-DFAB. In the pump-probe data, the covariance maps at very early delays show a significant increase in signal relative to the probe-only map due to the population of the S_2 electronic excited state by the 330 nm pulse. Increasing the pump-probe delay leads to a decrease in the intensity within each covariance map, as seen earlier in the total ion yield. This is because the excited molecules have time to relax before the arrival of the probe pulse.

At delays greater than 5000 fs, the localized feature at around 180° spans a broader range of angles (an increase in FWHM of approximately 10°) and is not as strongly confined as in the probe-only case. The emission of F^+ ions at a broader range of angles may be a signature of *cis*-DFAB (from *trans-cis* photoisomerization) with/without vibrationally hot *trans*-DFAB after relaxation to the ground electronic state. In the former case, it is predicted that the appearance of *cis*-DFAB would generate signatures at around 120° and 240° in the $Cov(F^+, F^+)$ two-fold covariance map for relatively large pump-probe delays. While in the latter case, the fluorines are expected to have back-to-back emissions but with a broader angular distribution in the pump-probe data relative to the probe-only data.

In the perpendicular case, the probe-only map also shows a back-to-back emission of the two F^+ ions with respect to each other. This is due to the $N=N$ double bond in *trans*-DFAB as shown by the sketch in the figure. A similar rise in signal is also seen in the very early pump-probe delays relative to the probe-only data, which is accompanied

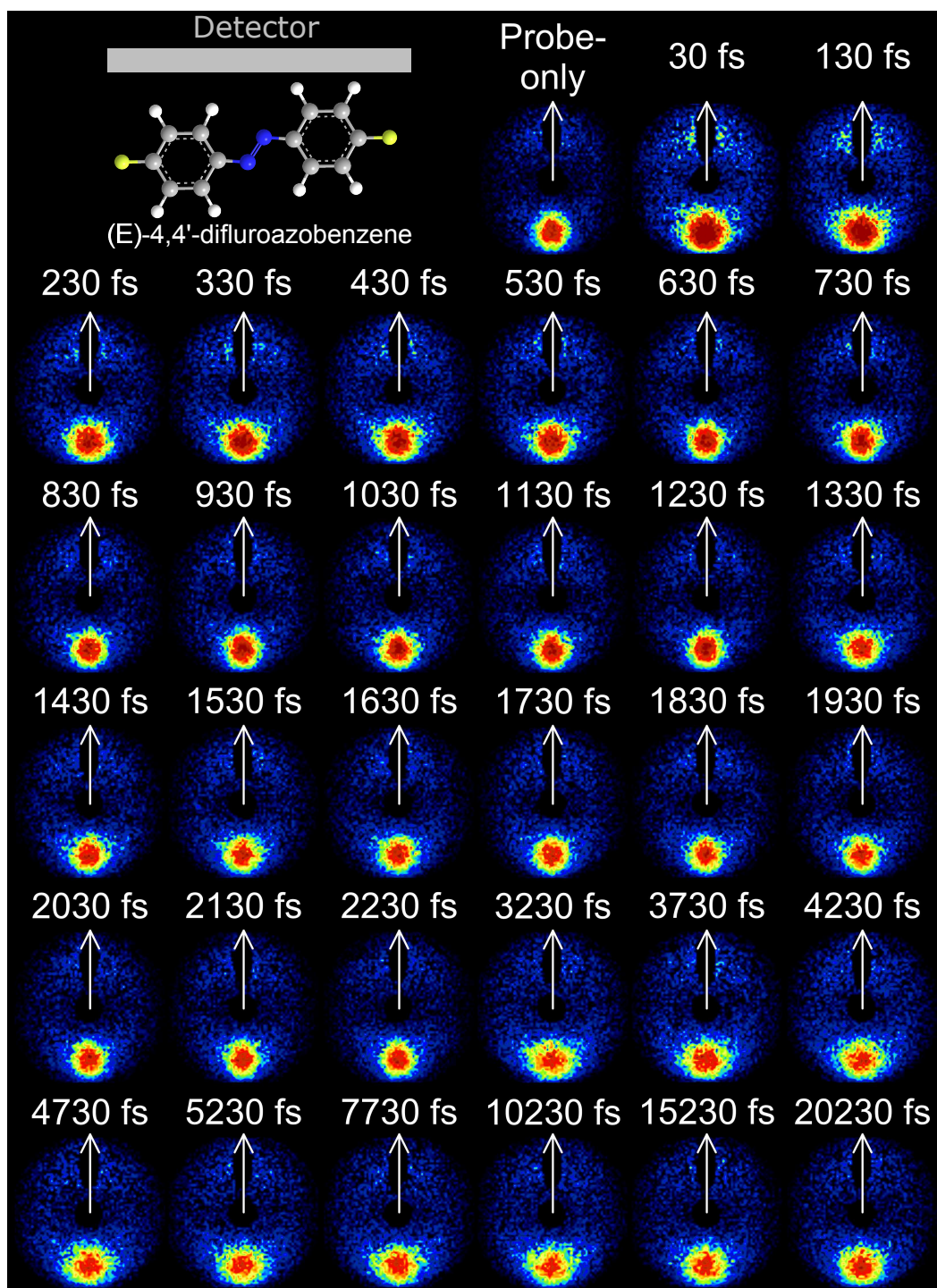


Figure 6.5: The experimental two-fold covariance maps, $Cov(F^+, F^+)$, recorded by the PImMS1 camera in the parallel configuration are presented for unaligned 4,4'-difluoroazobenzene molecules following UV-pump and strong-field ionization by 330 nm and 800 nm pulses, respectively. Here, one of the fluorines is chosen as the reference ion and the other is shown as the plotted ion in each map. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map. The labels above each map indicate the probe-only and the corresponding pump-probe delay that each map corresponds to. The maps were normalised to the maximum intensity of the probe-only map.

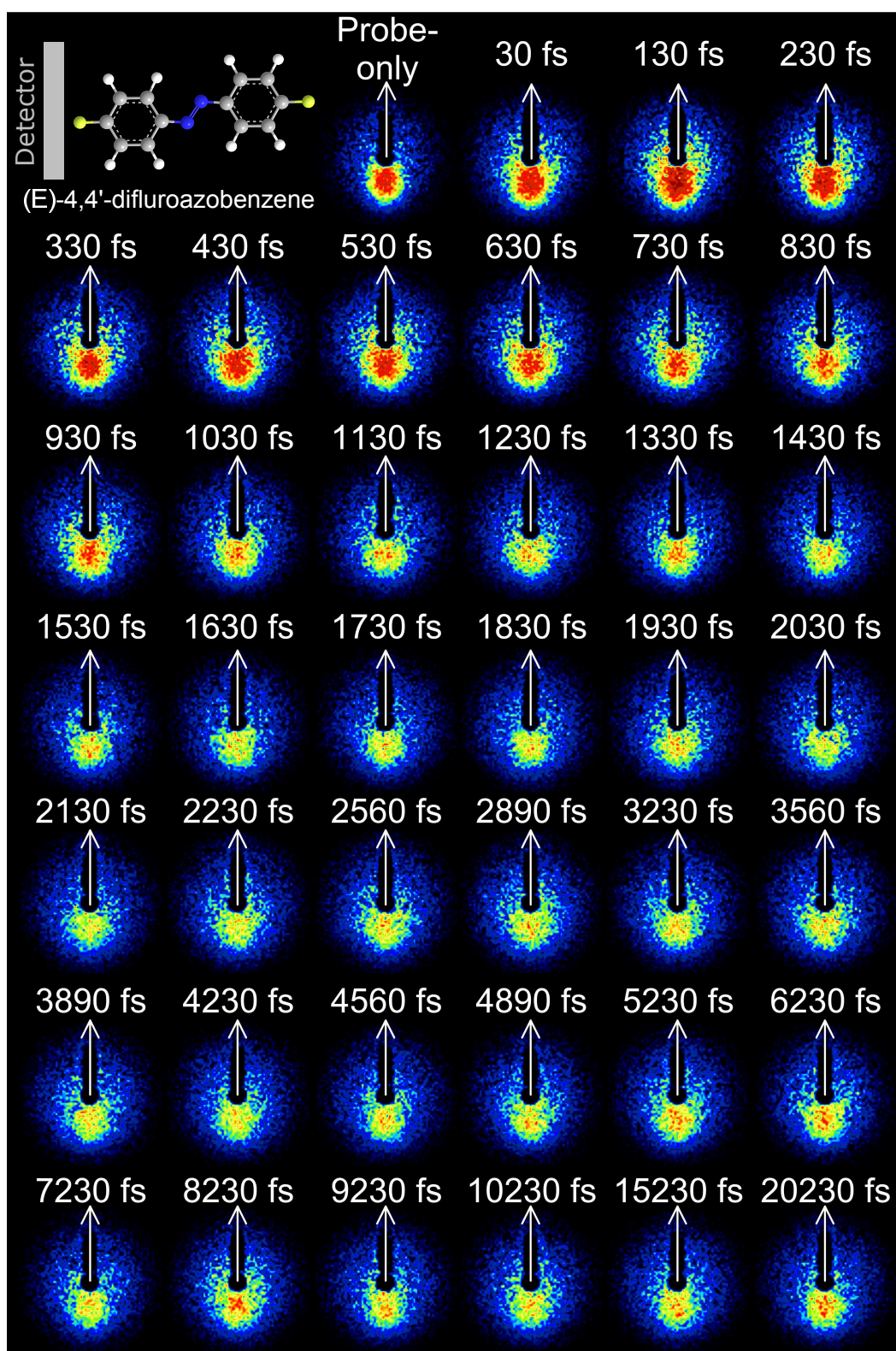


Figure 6.6: Similar to Figure 6.5 but for the perpendicular configuration. As in Figure 6.5, one of the fluorines is chosen as the reference ion and the other is shown as the plotted ion in each map. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map. The labels above each map indicate the probe-only and the corresponding pump-probe delay that each map corresponds to. The maps were normalised to the maximum intensity of the probe-only map.

by a decrease in intensity with increasing delay. Interestingly, the intensity of the localized feature at 180° in the pump-probe data becomes less intense than that of the probe-only case at time delays longer than 600 fs. The *cis*-DFAB molecule in the perpendicular geometry is expected to show features at a very broad range of angles in the $Cov(F^+, F^+)$ map since the molecule is free to rotate around the polarization axis of the probe pulse (*i.e.* along the ToF axis). Although the feature at approximately 180° in the pump-probe data is not as well confined or intense as in the probe-only data, the interpretation of the perpendicular pump-probe data is still inconclusive.

Delay-dependent angular distribution maps are shown in Figure 6.7 for the parallel and perpendicular configurations in panels (a) and (b), respectively. As seen earlier in the covariance maps, the large signal at very early delays quickly decreases in intensity with increasing delay in both configurations. The angular distributions for a selection of pump-probe delays are shown in panels (c) and (d) for both configurations which are also accompanied by the probe-only distribution. All distributions were normalised to their corresponding maximum intensity. In both configurations, the pump-probe distributions are all broader than the probe-only data, particularly in the perpendicular case. The angular distributions for the parallel and perpendicular geometries are broader by 10° (FWHM) and 30° (FWHM), respectively, relative to the probe-only distribution. This broadening of angular distributions, as stated earlier, could be a signature of *cis*-DFAB with/without vibrationally hot *trans*-DFAB in the S_0 state. In the following section, details are given for a probe-only subtraction method that was applied to the pump-probe covariance data to account for contributions from unexcited *trans*-DFAB molecules.

6.3.3 Probe-Only Subtracted Two-Fold Covariances

The probe-only data corresponds to the Coulomb explosion of *trans*-DFAB molecules in the S_0 state. In the pump-probe data, only a limited proportion ($< 50\%$) of *trans*-DFAB molecules are excited into the S_2 state by the 330 nm pulse. It is possible to subtract away the contributions from unexcited *trans*-DFAB molecules by subtracting the probe-only two-fold covariance map from each pump-probe covariance map.

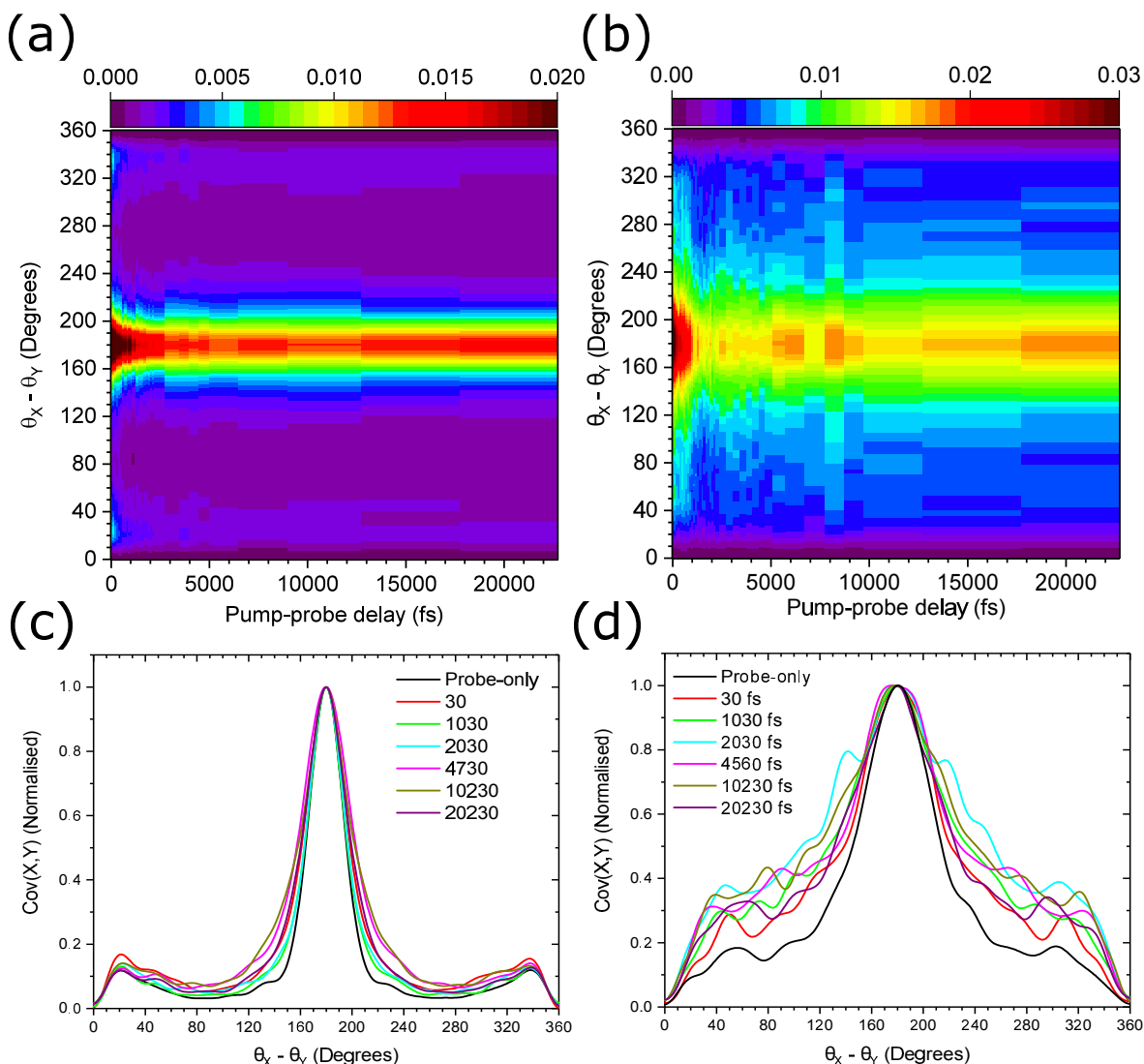


Figure 6.7: Delay-dependent angular distribution maps extracted from the $\text{Cov}(F^+, F^+)$ maps in the (a) parallel and (b) perpendicular configurations as shown in Figures 6.5 and 6.6. A selection of angular distributions are shown for pump-probe data (coloured traces) alongside the probe-only delays (black trace) for both (c) parallel and (d) perpendicular configurations. The distributions in panels (c) and (d) were normalised to their respective maximum intensity.

The probe-only data must be correctly scaled to properly account for the amount of unexcited *trans*-DFAB molecules in the data. A good scaling factor will not lead to the over-subtraction of the pump-probe data and create negative intensity in the subtracted maps. The subtracted covariance maps could reveal underlying structures that may correspond to either *cis*-DFAB, excited *trans*-DFAB or both.

Figure 6.8 shows the probe-only subtracted data for the parallel and perpendicular configurations in panels (a) and (b), respectively. Only positive intensities are shown in each map. The maps in each column correspond to the sum of subtracted data for

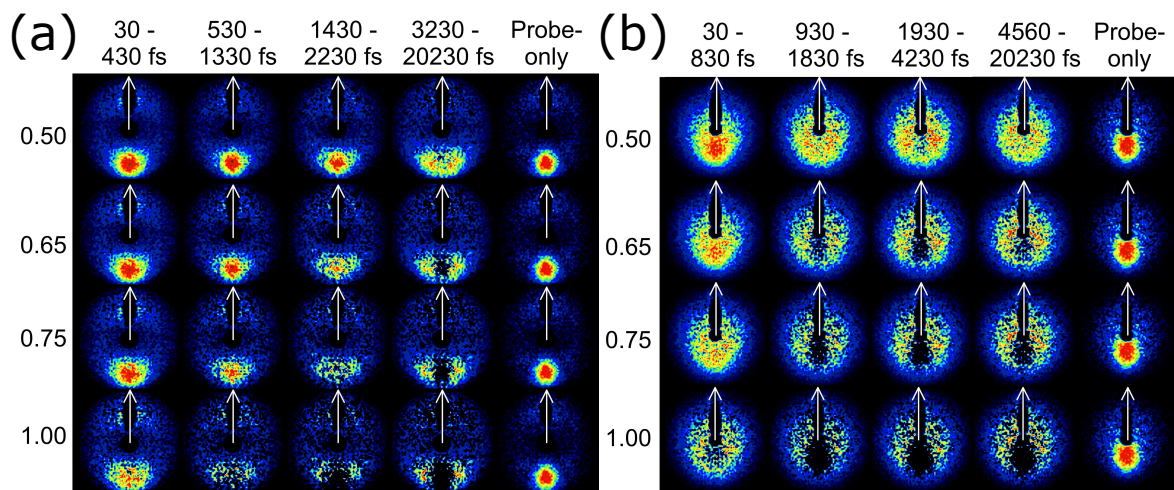


Figure 6.8: The probe-only subtracted $Cov(F^+, F^+)$ maps for the (a) parallel and (b) perpendicular configurations at a selection of pump-probe delays which are accompanied by the probe-only data. In the pump-probe data, the subtracted maps were summed for the corresponding delay range shown at the top of each panel. The probe-only data was scaled by the factor indicated on the left hand-side of each panel. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map.

four ranges of pump-probe delays, while the final column shows the probe-only data. In each row, the scaling factor that was applied to the probe-only data is indicated. The scaling factor has limiting values of between 1.0 and 0.5. The maximum value of 1.0 corresponds to the case where none of the *trans*-DFAB molecules are excited by the 330 nm pulse, and therefore 100% of molecules that are detected would be unexcited *trans*-DFAB. While the minimum value of 0.5 corresponds to the case where up to 50% of all *trans*-DFAB molecules could be optically pumped.

In both the parallel and perpendicular configurations, the long-time data (fourth column) shows the most significant change as a function of the scaling factor. Increasing the scaling factor from 0.5 to 1.0 leads to a significant reduction in intensity at approximately the same region as the localized feature in the probe-only map (final column). This suggests that an over-subtraction has occurred. In the long-time limit, the subtracted maps (fourth column) are significantly different to the corresponding probe-only map (final column). The biggest difference between the subtracted and the probe-only data is observed in the perpendicular configuration. In this configuration, the distinct feature at 180° in the probe-only map is only present in the 30-830 fs subtracted map that uses a scaling factor of 0.5. In the long-time limit, the subtracted

maps show the ejection of both fluorines at a very broad range of recoil angles. The over-subtraction of the probe-only data is particularly evident by the appearance of a “hole” in the subtracted maps at 180° with a scaling factor of 1.0 at delays of 930 fs and above.

The delay-dependent angular distribution maps of the probe-only subtracted data for the parallel geometry is shown in Figure 6.9 for all four scaling factors. Regions of black intensity correspond to negative intensity values and thus over-subtraction of the probe-only data. In all four maps, the large intensity at early delays quickly decreases

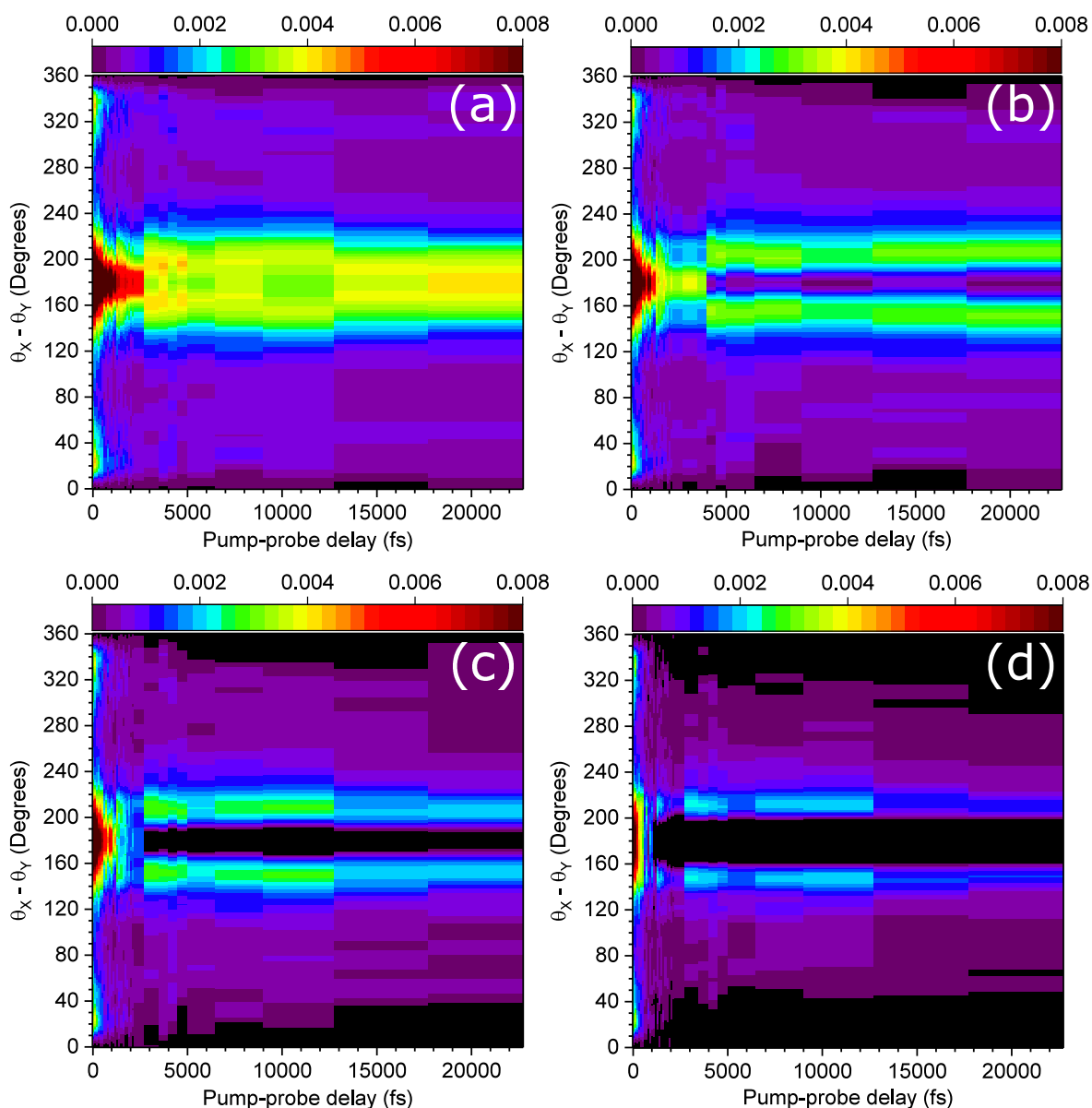


Figure 6.9: Delay-dependent maps of angular distribution for probe-only subtracted data in the parallel configuration using the following probe-only scaling factors: (a) 0.50, (b) 0.65, (c) 0.75, and (d) 1.00. Regions of black intensity indicate negative $Cov(F^+, F^+)$ values that are a result of the probe-only subtraction method.

with increasing delay in the first 1000 fs, which is characteristic of the de-population of the electronic excited states. The signal at around 160 - 200° decreases as the scaling factor increases from 0.50 to 1.00 , creating a “hole” in signal that becomes negative at 0.75 and above. Thus, scaling factors of 0.75 and above leads to an over-subtraction of the probe-only data from the pump-probe data, while the scaling factor of 0.65 and above generates only positive intensity values. Although there is significant over-subtraction of the probe-only data in the case of a scaling factor of 1.00 , there still does exist positive covariances at approximately 150° and 210° .

The angular distribution for a selection of pump-probe delays (coloured traces) is shown for each of the four scaling factors in Figure 6.10 which are accompanied by the scaled probe-only distribution (black dashed trace). Panel (a) corresponds to

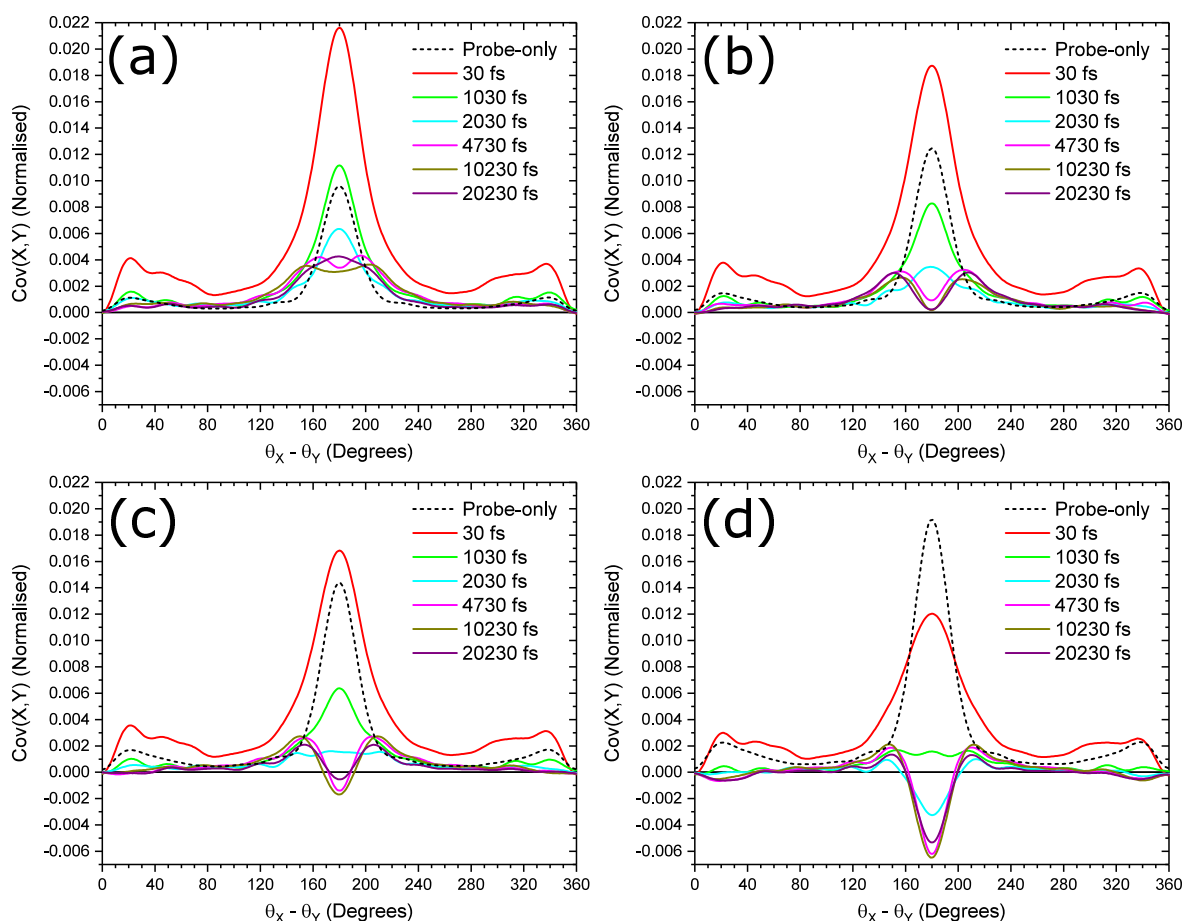


Figure 6.10: A selection of angular distributions in the parallel geometry are shown for probe-only subtracted pump-probe data (coloured traces) corresponding to the data shown in Figure 6.9. Distributions are shown for the following probe-only scaling factors: (a) 0.50 , (b) 0.65 , (c) 0.75 , and (d) 1.00 . The scaled probe-only data (black dashed trace) is also shown.

the scaling factor of 0.50, and shows distributions that are all positive. The large intensity at early delays quickly decreases with increasing delay. In the long-time limit of above 10 ps, a distribution with two faint peaks at approximately 150° and 210° are observed as a result of the probe-only subtraction process. These two peaks become more pronounced with the larger scaling factor of 0.65 as shown in panel (b), where all distributions are still positive. In the case of 0.75 and 1.00 in panels (c) and (d), the angular distributions now contain negative intensities at approximately 180° . Thus, using scaling factors of 0.75 and above leads to an over-subtraction of probe-only data from the pump-probe data, as seen qualitatively earlier in Figure 6.9. The double-peak feature still exist at approximately 150 and 210° , although these are slightly less intense than in panel (b). It should be noted that the subtraction process may artificially create this double-peak feature, so caution must be taken to not over-interpret this feature.

The delay-dependent angular distribution maps for the subtracted data in the perpendicular configuration are shown in Figure 6.11 for the same four scaling factors of 0.50, 0.65, 0.75, and 1.00 in panels (a) - (d), respectively. Here, the probe-only subtraction using scaling factors of 0.75 and 1.00 also lead to the over-subtraction of probe-only data from the pump-probe data, as seen for the parallel data. In the case of 0.65, a small hole is generated at an angle of 180° , and leads to the generation of two localized features peaking at approximately 90° and 270° due to the probe-only subtraction process. In the 0.50 case, the F^+ ions appear to be ejected at a broad range of angles above 1000 fs.

Angular distributions in the perpendicular geometry from a selection of pump-probe delays (coloured traces) are shown in Figure 6.12 which are accompanied by the scaled probe-only distribution (black dashed trace). In the long-time limit, the subtracted distributions show two broad features that are roughly peaked at 90° and 270° using scaling factors of 0.65 and above. While a broad angular distribution is observed with a scaling factor of 0.50.

This may be due to the appearance of the *cis* isomer in the perpendicular geometry which is also expected to emit the fluorines at a broad range of recoil angles. In contrast, the probe-only distribution has a local maximum at 180° , which is expected as only

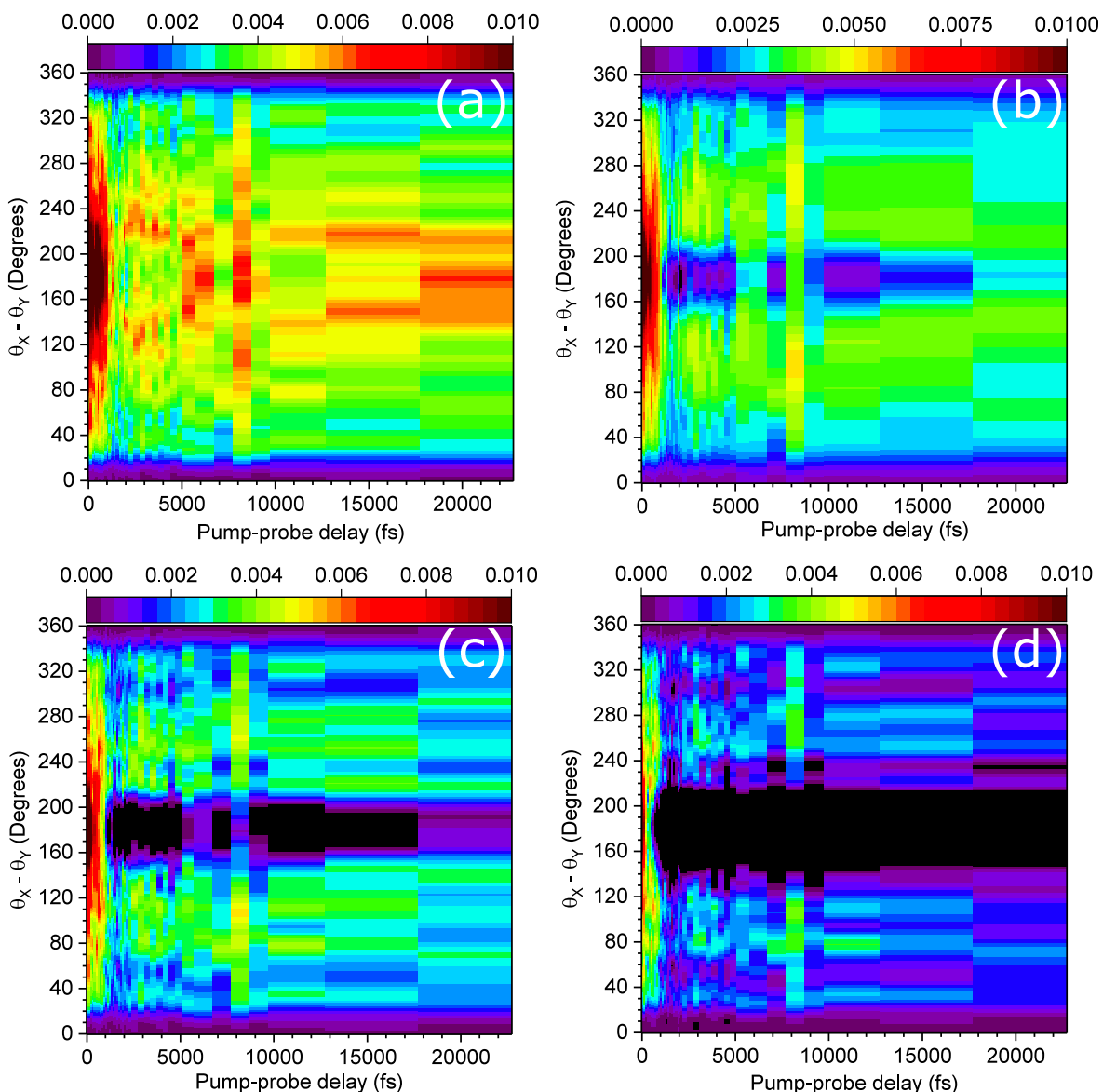


Figure 6.11: Similar to Figure 6.9 but for the perpendicular configuration. Probe-only subtracted data are shown for the following probe-only scaling factors: (a) 0.50, (b) 0.65, (c) 0.75, and (d) 1.00. Regions of black intensity indicate negative $Cov(F^+, F^+)$ values that are a result of the probe-only subtraction method.

trans-DFAB is present in the probe-only data.

Although there is some evidence for the *cis* isomer in the subtracted data, these are still not conclusive enough to definitively support the appearance of *cis*-DFAB. It is also possible that vibrationally hot *trans*-DFAB is present in the subtracted data. It is currently not possible to definitively assign the time-dependent feature in the subtracted data to *cis*-DFAB with/without vibrationally hot *trans*-DFAB. To further aid the interpretation of the subtracted data, a comparison between experimental and simulated results is shown in the following section.

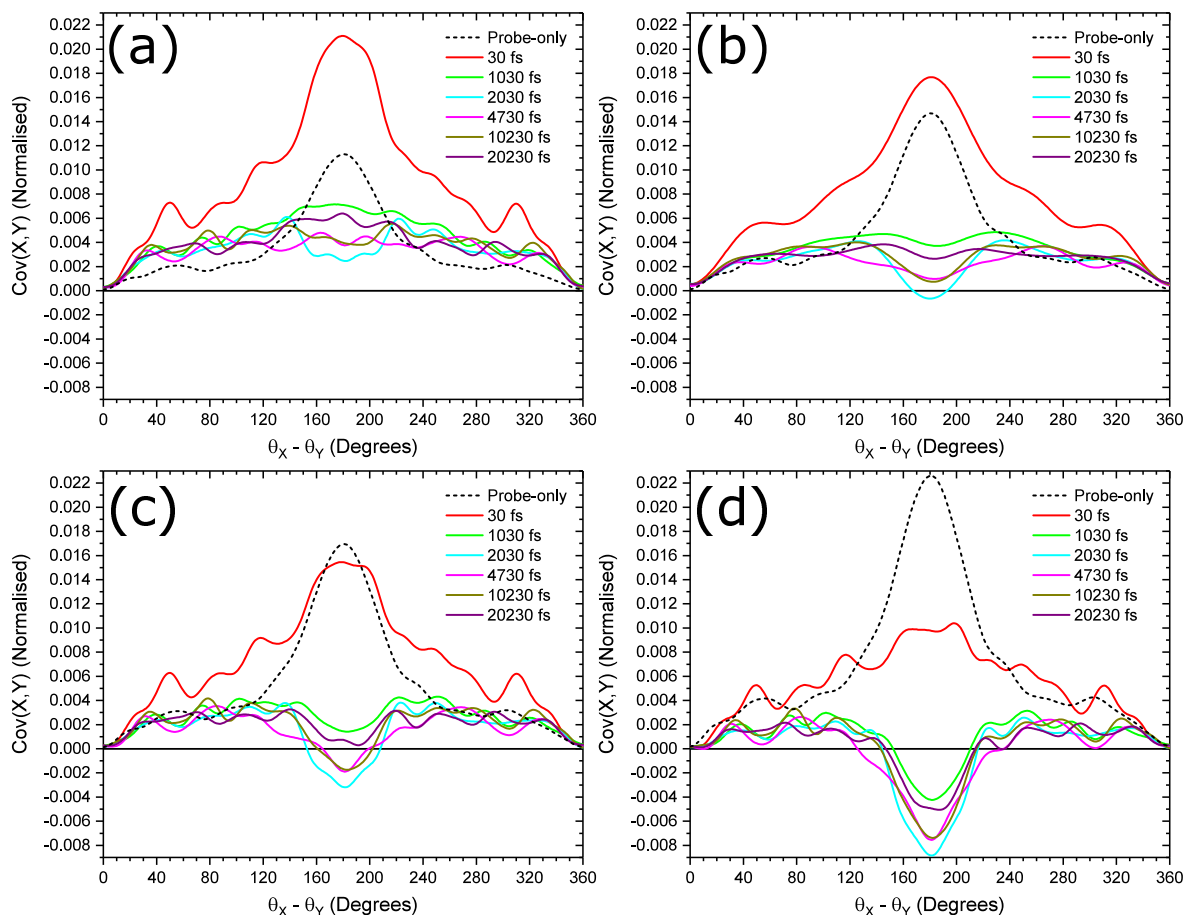


Figure 6.12: Similar to Figure 6.10 but for the perpendicular configuration. Distributions are shown for the following probe-only scaling factors: (a) 0.50, (b) 0.65, (c) 0.75, and (d) 1.00. The scaled probe-only data (black dashed trace) is also shown.

6.4 Simulations

In this section, simulated results from the Coulomb explosion of *trans*-DFAB and *cis*-DFAB molecules are presented. The simulated $Cov(F^+, F^+)$ two-fold covariance maps for the *cis*- and *trans*-DFAB isomers are shown in Figure 6.13 in the parallel and perpendicular configurations. Each column of maps corresponds to the average charge placed on each molecule in the simulation, as indicated by the labels at the top of the figure. For comparison, the corresponding experimental maps from the probe-only and subtracted pump-probe data are shown on the right hand side of the same figure in both configurations. The subtracted data shown corresponds to a scaling factor of 0.65 at large pump-probe delays (> 3000 fs).

In the parallel geometry, the simulated images corresponding to an average charge of +10 show the best qualitative agreement with the experimental maps. While in

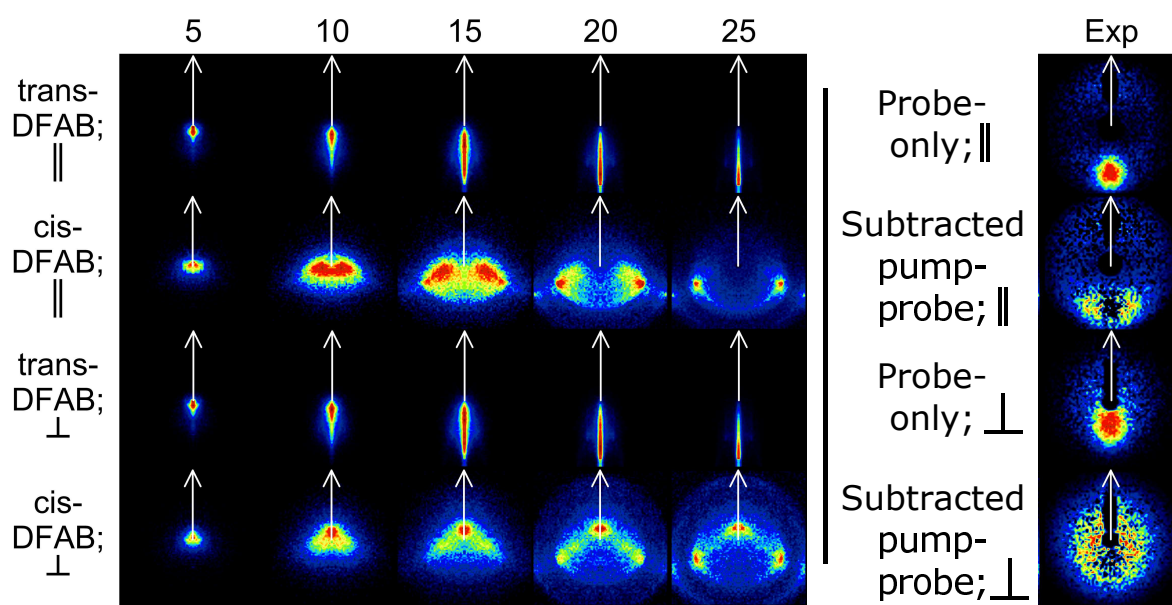


Figure 6.13: Simulated two-fold covariance maps, $Cov(F^+, F^+)$, for *trans*- and *cis*-DFAB molecules in the parallel and perpendicular geometries. Here, one of the fluorines is chosen as the reference ion and the other is shown as the plotted ion in each map. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map. The average charge states of the molecule used in the simulation are indicated by the labels above the maps. On the right hand side, the probe-only and subtracted pump-probe data are shown for both configurations. The latter data corresponds to a scaling factor of 0.65 at large pump-probe delays (>3000 fs).

the perpendicular case, a +15 charge in the simulated data showed the best agreement with the experimental data. The angular distribution of each simulated covariance map is presented in Figure 6.14, where each panel corresponds to each row of Figure 6.13. The angular distributions were normalised to their corresponding maximum intensity. In the simulated results for *trans*-DFAB, an increase in the average charge leads to a narrower angular distribution in both configurations. This is due to stronger Coulomb repulsion between ions that leads to the emission of two F^+ ions with distinct recoil angles. Thus, a higher average charge better reflects the direction of the C-F bond axes in DFAB at the moment of initial ionization by the 800 nm pulse.

In the *trans*-DFAB case, the simulated angular distribution in the parallel geometry for an average charge of +10 (green solid trace) has the closest agreement to the experimental probe-only (black dashed trace) distribution, as shown in Figure 6.14(a). In the perpendicular case, the experimental distribution (black dashed trace) has the closest agreement with the +5 simulated distribution (red solid trace), as shown in

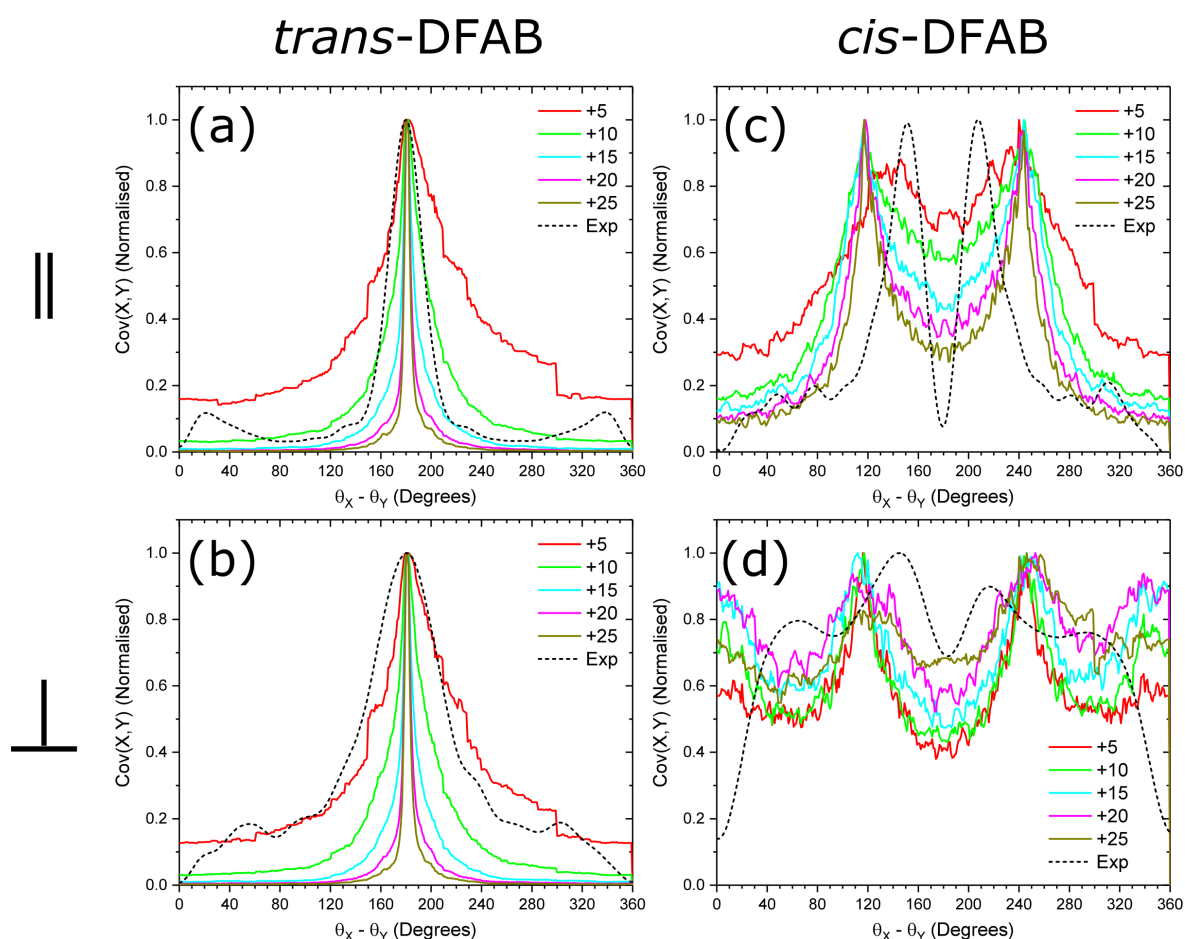


Figure 6.14: The angular distributions of the simulated maps (coloured solid traces) are shown in Figure 6.13 for the *trans*-DFAB (first column) and *cis*-DFAB (second column) molecules. These are accompanied by the corresponding experimental data (black dashed trace). Panels (a) and (c) correspond to the parallel configuration, while the perpendicular configuration is shown in panels (b) and (d). Each distribution has been normalized to its corresponding maximum intensity.

Figure 6.14(b). This suggests that the true charge on the molecule is somewhere between +5 and +10 during the Coulomb explosion of *trans*-DFAB molecules.

In the simulation of *cis*-DFAB, the simulated angular distributions (coloured solid traces) do not have a conclusive agreement with the probe-only subtracted data (black dashed trace). In the parallel case, the simulated distributions appear at peak recoil angles of approximately 120° and 240°, which is approximately 30° smaller than in the subtracted experimental distribution, as shown in Figure 6.14(c). In the perpendicular geometry, the simulated distributions contain peak recoil angles at 0°, 115° and 245°, as shown in Figure 6.14(d). A relatively large discrepancy also exists in this geometry between the subtracted experimental and simulated angular distributions. No conclusive agreement is seen between the simulated data on *cis*-DFAB and the probe-only

subtracted experimental data to definitively support the detection of the *cis* isomer.

6.5 Conclusions and Future Work

In this chapter, the *trans-cis* photoisomerization of (E)-4,4'-difluoroazobenzene was attempted using 330 nm pump and 800 nm probe optical pulses. A significant increase in the total ion yield was observed at a pump-probe delay of approximately 30 fs when compared to the probe-only data, which decreased in intensity with increasing pump-probe delay. The time constant of ~ 600 fs was extracted from the exponential decay in signal, which corresponds to the $S_0 \leftarrow S_1$ relaxation pathway [293]. The measured time constant is also close to the value of 420 fs measured by Stolow and coworkers on jet-cooled azobenzene at 330 nm [294], which was reassigned as the lifetime of S_1 by Bandara and Burdette [293]. Stolow and coworkers also found the $S_1 \leftarrow S_2$ internal conversion lifetime to be 170 fs [294], which did not appear in the measurements presented in this chapter due to the relatively large temporal resolution of 120 fs, given by the measured cross-correlation of the two pulses.

In the two-fold covariance maps, $Cov(F^+, F^+)$, the angular distributions for the parallel and perpendicular geometries were broader by 10° (FWHM) and 30° (FWHM), respectively, relative to the probe-only feature at 180° . This broadening of angular distributions could be due to *cis*-DFAB with/without vibrationally hot *trans*-DFAB molecules in the S_0 state. A probe-only subtraction method was applied to remove the contribution of unexcited *trans*-DFAB molecules to the pump-probe data. The probe-only subtraction method involves scaling down the probe-only data by a particular factor that is related to the proportion of molecules that were left unexcited after interaction with the pump pulse. The scaling factor had the limiting values of 0.5 and 1.0. In both the parallel and perpendicular geometries, the scaling factor of 0.75 and above lead to negative values in the angular distribution of subtracted data which is due to the over-subtraction of the probe-only data from the subtracted data.

A good agreement was observed between the simulated data for *trans*-DFAB and the probe-only experimental data, confirming that only *trans*-DFAB molecules were

present in the probe-only measurements. The simulated data corresponding to an average charge of between +5 and +10 was found to best match the probe-only experimental data. The simulated data for the *cis*-isomer in the parallel geometry contained two local maxima at approximately 120° and 240° , which was approximately 30° smaller than in the experimental subtracted distribution. In the perpendicular geometry, the simulated distributions contained peak recoil angles at 0° , 115° and 245° , which were also significantly (30°) different to that of the subtracted data. No conclusive agreement is seen between the simulated data on *cis*-DFAB and the probe-only subtracted experimental data to suggest that the *cis* isomer was present in the experimental pump-probe measurements. The pump-probe signal that appears at large pump-probe delays could be from *cis*-DFAB with/without vibrationally hot *trans*-DFAB molecules. It is clear that the accurate subtraction of the 'background' (unexcited *trans*-DFAB) signal in the pump-probe data is crucial in these types of experiments which investigate ultrafast structural dynamics following the population of excited electronic states and subsequent relaxation to the ground electronic state.

Several improvements may be possible to implement into future time-resolved pump-probe experiments that implement the probe-only subtraction method of covariance images. Firstly, recording the probe-only and pump-probe data on alternate shots at half the repetition rate of the experiment will lead to a more reliable probe-only subtraction. In the work presented here, the probe-only data were recorded only a few times during the acquisition of the pump-probe data. At the time of the experiments it was not possible to implement the alternate shot method of recording probe-only and pump-probe data. Although the angular distribution and features will not change in the probe-only data, the intensity of the signal that is present may fluctuate during long periods of data recording that span several hours. Secondly, replacing one of the fluorines with another substituent group, such as chlorine or the cyano (-CN) group, will lead to covariance images that do not have the region at around 0° masked due to autocovariances. This will in particular increase the quality of the covariance images in the perpendicular geometry. Thirdly, impulsively aligning the molecules will improve the correlations that are seen in the unaligned data shown in this work. The non-

adiabatic method of alignment will also not influence the excited state dynamics in the molecule following interaction with the 330 nm pump pulse. While adiabatic alignment could perturb and change the electronic structure of *trans*-DFAB. It would be very interesting to repeat this *trans-cis* isomerization experiment with the *trans*-stilbene derivative, since the *cis*-stilbene is commercially available and therefore probe-only data of the *trans*-stilbene as well as the *cis*-stilbene molecules can be separately recorded. This will then confirm the start and end point of the *trans-cis* isomerization reaction of *trans*-stilbene, and can confirm whether isomerization has occurred. If so, then the photoisomerization dynamics can be imaged on the femtosecond timescale.

In the Coulomb explosion imaging work presented in this thesis so far, the Coulomb explosion of a molecule was induced by strong-field ionization using an 800 nm Ti:Sa laser pulse. Inner-shell ionization can also induce a Coulomb explosion in a molecule, as discussed in Section 4.3 in Chapter 4. An investigation into the similarities and differences in the Coulomb explosion of molecules induced by strong-field ionization and inner-shell ionization is presented in the following chapter.

Chapter 7

Coulomb Explosions *via*

Strong-Field and Inner-Shell

Ionization

7.1 Introduction

This chapter presents results from the Coulomb explosion of adiabatically aligned and mixed-field oriented 2,6-difluoriodobenzene (2,6-DFIB, $\text{C}_6\text{H}_3\text{F}_2\text{I}$) molecules initiated by strong-field ionization (using high-intensity femtosecond 800 nm Ti:Sa pulses) and multi-photon inner-shell ionization (using extremely intense and ultrashort 11.6 nm free-electron laser (FEL) pulses). An investigation into the angular and kinetic energy distributions of the recoil fragments is carried out to gauge how similar or different the two ionization schemes are in the Coulomb explosion of 2,6-DFIB.

The 2,6-DFIB molecule was chosen because it has a very high polarizability of $\alpha_{zz} = 21.3 \text{ \AA}$, $\alpha_{yy} = 14.5 \text{ \AA}$, and $\alpha_{xx} = 8.5 \text{ \AA}$, where α_{zz} , α_{yy} , α_{xx} are the diagonal elements of the polarizability tensor. Here, the z-axis is defined as parallel to the C-I axis, the y-axis perpendicular to the z-axis in the molecular plane, and the x-axis is perpendicular to the molecular plane [158]. Thus, the most polarizable axis (MPA) in 2,6-DFIB is parallel to the C-I axis, and the second most polarizable axis (SMPA) lies

in the molecular plane. Consequently, a linearly polarized pulse can adiabatically align the molecule along the MPA to achieve 1D-alignment as shown in Figure 4.4(b) in Chapter 4. Furthermore, an elliptically polarized pulse can align the molecule's MPA and SMPA along the major and minor axes, respectively, of the propagating light pulse to achieve 3D-alignment, as shown in Figure 4.4(c) of Chapter 4.

The laser-induced molecular alignment and mixed-field orientation [62, 158, 306, 307] of difluoroiodobenzene (DFIB) have been studied previously by several authors through Coulomb explosion imaging and strong-field ionization with an 800 nm Ti:Sa pulse. Nevo *et al.* used an elliptically polarized nanosecond pulse to adiabatically (field-induced) 3D-align 2,6-DFIB molecules [158]. The authors also demonstrated the orientation of aligned molecules using a combination of optical and static fields [158], and they also showed an improvement in the degree of alignment and orientation by selecting the rotationally coldest molecules using a deflector [158].

Viftrup *et al.* used two linearly polarized pulses to 3D-align 3,5-DFIB molecules: a nanosecond (long) pulse and a femtosecond (short) pulse. The long pulse aligned the most polarizable axis of the molecule along the polarization vector of the laser pulse, while the short pulse was polarized orthogonal to the long pulse in order to control the rotation of the molecule about the aligned axis. Ren *et al.* used a sequence of three elliptically polarized femtosecond pulses to achieve non-adiabatic (field-free) 3D-alignment of 3,5-DFIB molecules, with each subsequent alignment pulse leading to an improvement in the degree of alignment of the molecules [307].

The fragmentation dynamics following inner-shell ionization of 2,6-DFIB and 3,5-DFIB have been studied by an electron-ion-ion coincidence experiment at 107 eV [291]. Rolles and coworkers were able to distinguish the two isomers experimentally through the momentum correlations between I^+ and F^+ ions. They also showed, through classical Coulomb explosion simulations, a step-wise fragmentation in both molecules which generated I^+ , F^+ and a third charged co-fragment over a several hundred femtosecond timescale [291].

In the work presented in this chapter, the laser-induced alignment and orientation of 2,6-difluoroiodobenzene is investigated using the PImMS1 camera during a free electron

laser beamtime with limited experimental time (2 weeks).

7.2 Experimental Methods

A brief overview of the experimental parameters used are given in this section, with a detailed discussion given in Chapter 2. The measurements presented in this chapter were recorded at a repetition rate of 10 Hz. A gas sample mixture of either methyl iodide or 2,6-difluoriodobenzene was seeded in neon (total gas mixture pressure of 20 bar), and expanded through the nozzle of the pulsed Even-Lavie valve to generate a molecular beam. The valve was triggered at a repetition rate of 10 Hz, limited by the in-house pump Ti:Sa laser.

The target molecule was adiabatically aligned with a 1064 nm alignment pulse which was generated with a Nd:YAG nanosecond laser. Strong-field ionization of molecules was avoided by keeping the intensity ($I_0 = 8 \times 10^{11} \text{ W cm}^{-2}$) of the alignment pulse low. An 800 nm (NIR) or 11.6 nm (XUV) pulse was used to ionize the target molecules. The pulses were generated with either the in-house Ti:Sa 10 Hz laser system or the FLASH free-electron laser (FEL), respectively. The XUV intensity ($3 \times 10^{13} \text{ W cm}^{-2}$) was determined by the highest pulse energy that was available at the requested pulse duration, while the NIR intensity ($2 \times 10^{14} \text{ W cm}^{-2}$) was set such that a similar ratio of I^+ and I^{2+} ion yields was observed in the NIR and XUV data in order to study comparable Coulomb explosion conditions.

The ions (electrons) generated by the probe pulse were extracted upwards (downwards) towards the ion (electron) detector in a double-sided VMI spectrometer [146, 174, 175]. The voltages applied to the electrostatic plates of the VMI spectrometer for the 800 nm and 11.6 nm measurements presented in this chapter are listed in Table 7.1. Although both ion and electron data were recorded at the same time, only the ion data is only presented in this chapter. The ion detector had a voltage difference of around 1750 V was applied across the MCPs, while a voltage difference of around 2400 V was used between the back face of the back MCP and the phosphor screen. Either a conventional CCD camera or PImMS1 camera captured the flashes of light

	V_{L1B}	V_{L2B}	V_{DTB}	V_{L1T}	V_{L2T}	V_{DTT}
800 nm	+613	+1592	+2132	-259	-1829	-1951
11.6 nm	+1160	+3209	+4271	-655	-3838	-361

Table 7.1: The $V_{L1B}/V_{L2B}/V_{DTB}/V_{L1T}/V_{L2T}/V_{DTT}$ voltages used in the 800 nm and 11.6 nm measurements presented in this chapter, given in Volts.

that were emitted from the back of the P47 phosphor screen.

7.3 Results and Discussion

A comparison of the ToF spectra, velocity-mapped ion images, and the kinetic energy distributions is made between the strong-field and inner-shell ionization. Although results from DFIB are mainly presented, a small set of 1D-aligned CH_3I data are initially presented in order to compare the ToF performance of the PImMS1 camera with the high-resolution direct readout of the MCP signal.

7.3.1 Time-of-Flight Analysis

Figure 7.1 shows the ion TOF spectra for 1D-aligned CH_3I after inner-shell ionization with an intense 11.6 nm XUV pulse recorded with the PImMS1 camera (black trace) and the direct readout of the MCP signal with a high-resolution digitizer (Acqiris, red trace). In the same figure, the corresponding velocity-mapped ion images (recorded with the PImMS1 camera) are shown, illustrating the ability of the PImMS1 camera to record all available (x, y, t) information for multiple fragments.

Although a significantly better resolved spectrum are generated by the direct readout of the MCP signal, the PImMS1 camera can still clearly distinguish between most of the relevant fragments. It should also be noted that all PImMS1 data presented in this chapter were not centroided, which would have otherwise improved the resolution of the PImMS1 ToF spectrum. The gas density in the molecular beam was kept sufficiently high to ensure good:signal in the photoelectron images, which in turn lead to a very high ion flux. Since the ion detector is usually run at very high voltages to maximize the ion detection efficiency, this lead to the problem of overlapping pixel clusters

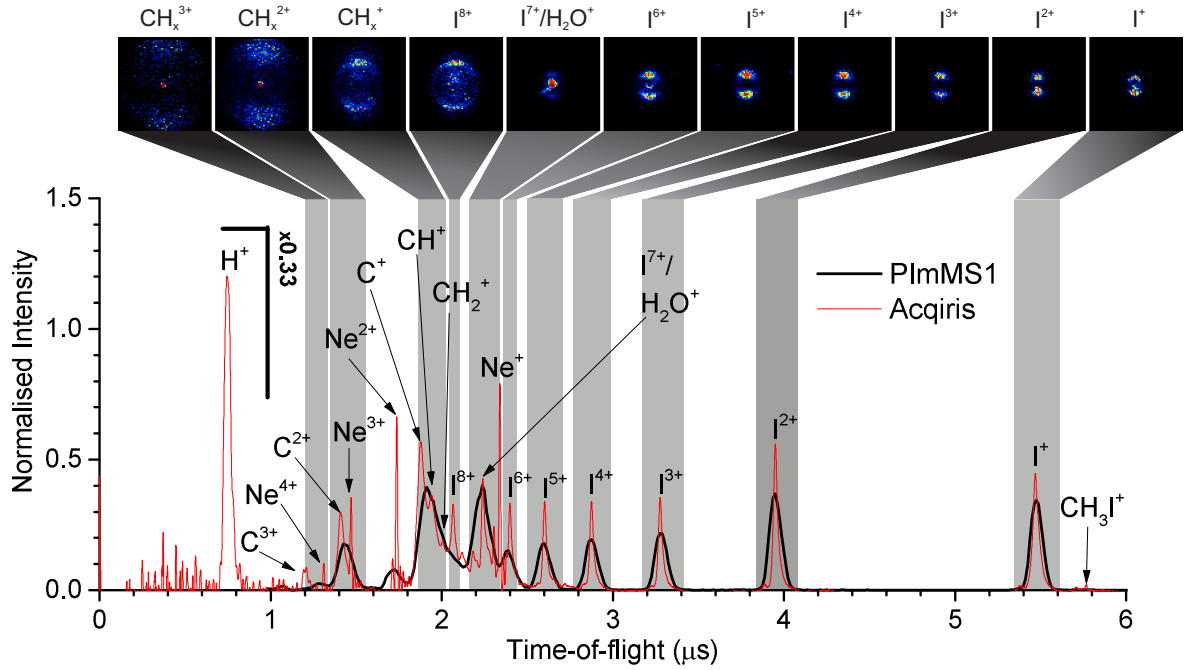


Figure 7.1: Time-of-flight spectra of ions formed after photoionization of 1D-aligned CH_3I with linearly polarized XUV photons at a photon energy of 107.8 eV recorded with the PImMS1 camera (black solid trace) and high-resolution Acqiris (red solid trace). Assignments for each peak are shown in the figure. The corresponding velocity-mapped ion images for the shaded ToF peaks, recorded with the PImMS1 camera, are presented above the ToF spectra. The intensity of fragments with a ToF of less than 1 microsecond were scaled by a factor of 0.33, and the PImMS1 camera was triggered just after the arrival of H^+ ions.

in the ion detector PImMS1 images. A compromise at the time of the experiment was to reduce the voltages applied to the ion detector to mainly produce mainly one-pixel ion clusters (75% of all clusters), and so the ion data was not suitable for centroiding. A significant amount of neon in various charge states is generated since neon has a relatively high absorption cross-section for photoionization at 107 eV. An appreciable amount of water is also ionized at this photon energy due to the significant valence ionization of water. The ToF traces for neon fragments recorded with the Acqiris are much more intense than in the corresponding PImMS1 traces. This is due to the very low kinetic energy that the various charge states of neon possess, which are consequently velocity-mapped onto the centre of the detector. Thus, the corresponding flash of light from the back of the phosphor screen only activates the central few pixels of the PImMS1 sensor. Since it takes the affected PImMS1 pixels ~ 100 ns to dissipate the charge in their photodiodes and to become sensitive again, any subsequent events that impact onto the pixel within this 100 ns window will not be detected. Consequently,

this leads to a significant reduction in the neon ToF profiles that were recorded with the PImMS1 sensor when compared to the MCP signal.

Figure 7.1 also shows many highly charged iodine fragments following the absorption of the XUV pulse by CH_3I . The iodine atom has a much higher total absorption cross-section for photoionization than the rest of the molecule, CH_3 , at 107 eV. In the case of I^{2+} , the inner-shell ionization of iodine and a single-Auger decay most likely leads to the loss of two electrons. It may also be possible that an iodine trication could be generated via an Auger cascade of a double-Auger decay process. Thus, the absorption of an XUV photon is initially strongly localized on the iodine site of the molecule [77, 81–83], with the absorption of one XUV photon leading to the net loss of at least two electrons in iodine. As the FEL operates at very high photon intensities, the molecule can therefore absorb multiple XUV photons which leads to the ejection of many electrons from the iodine site of the molecule to generate high charge states of iodine (I^{3+} to I^{8+}). Further evidence of these multi-photon effects is given later in the comparison of FLASH FEL (multi-photon XUV regime) and ALS synchrotron (single-photon XUV regime) ToF data of unaligned 2,6-difluoriodobenzene (DFIB).

Figure 7.2 compares the ion mass spectra of 1D-aligned DFIB molecules that have been Coulomb exploded through inner-shell ionization with an intense 11.6 nm pulse (green trace) and through strong-field ionization with an intense 800 nm pulse (black trace). Two additional spectra are shown for unaligned DFIB molecules following ionization by the XUV pulse that were recorded with the PImMS1 camera (red trace) and the direct readout of the MCP signal with a high-resolution digitizer (Acqiris, blue trace).

Just as seen earlier in CH_3I , the PImMS1 camera can resolve most of the relevant fragments particularly for $m/q > 30$ in DFIB, although the direct readout of the MCP signal generates a significantly better resolved mass spectrum (red and blue traces, respectively). At lower m/q , the PImMS1 camera can no longer sufficiently resolve the distinct peaks that are present in the MCP signal. The low KER fragments, such as OH^+ , H_2O^+ , Ne^+ , and parent^+ , have a significant reduction in their mass spectrum profiles recorded by the PImMS1 sensor when compared to the MCP signal due to

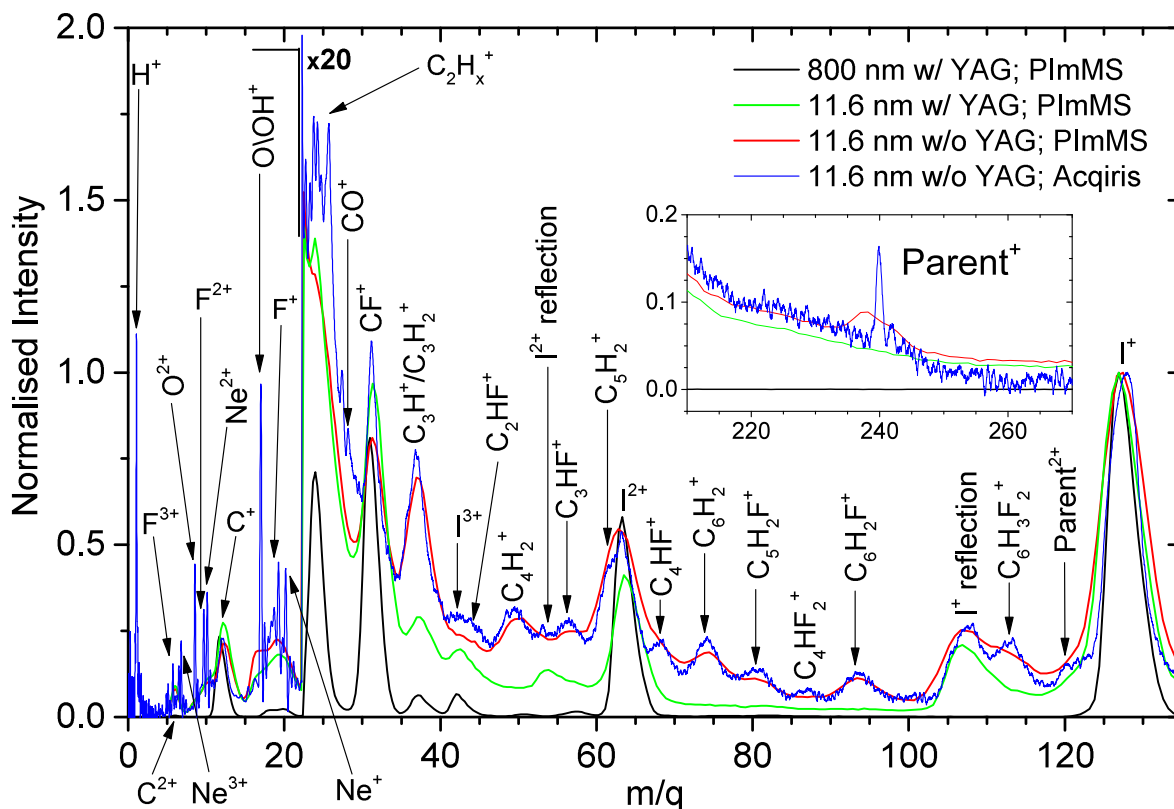


Figure 7.2: Ion time-of-flight mass spectra of DFIB after strong-field ionization with an intense 800 nm pulse (black line) and with an intense 11.6 nm XUV pulse (green and red lines), as recorded with the PImMS1 camera. The XUV spectra are shown with (green) and without (red) the presence of the Nd:YAG alignment pulse, and are also compared to the spectrum obtained from directly reading out of the MCP signal with a high-resolution digitizer (blue). The spectra are normalized to the maximum of the I^+ peak and have been scaled up by a factor of 20 for $m/q > 22$. The inset shows the m/q -region of the parent ion.

the temporary saturation of the central few pixels. This is due to the same reasons given earlier for neon ions in 1D-aligned CH_3I molecules probed with an XUV pulse. The Nd:YAG pulse fragments most of the larger molecular fragments including the parent ion (see inset) when comparing the spectra recorded with and without the Nd:YAG pulse present (red and green traces, respectively). The resulting spectrum in the presence of the Nd:YAG pulse is dominated by I^{n+} (with $n = 1, 2, 3$) and small carbon-containing fragments, which have been previously observed [159].

Several differences exist between the inner-shell ionization of DFIB and CH_3I . In DFIB, many more larger molecular fragments are present in its corresponding unaligned ToF trace, while the ToF trace of CH_3I is dominated by various charge states of iodine. This is because in the bigger molecule (DFIB), the DFB co-fragment can take up a lot

more charge, and the charges can spread to more fragments that generate ions with smaller charges. In work by Erk *et al.*, they observed that a bigger molecule lead to smaller charge states of ions following inner-shell ionization [308].

In DFIB, largely similar ion mass spectra are generated from the NIR and XUV pulses (black and green traces, respectively) even though the ionization pathways induced by the two pulses are significantly different. At the intensities used for the NIR ($I_0 \sim 2 \times 10^{14} \text{ W cm}^2$) and the XUV ($I_0 \sim 3 \times 10^{13} \text{ W cm}^2$) pulses, a large contribution of I^+ and I^{2+} ions exist in both spectra (black and green traces), however, significantly more I^{3+} ions are generated with the XUV than with the NIR pulse. A larger contribution from F^+ , F^{2+} and small carbon containing fragments are also present in the 11.6 nm spectrum, suggesting a generally higher degree of ionization than with the 800 nm pulses at the given intensity. It should be noted that the comparisons made here between the NIR and XUV are only valid at these intensities as strong-field ionization with the NIR pulse is much more strongly dependent on the photon intensity than ionization with the XUV pulse, since the former leads to a significant deformation of the Coulombic potential, as detailed in Chapter 4.

In the 11.6 nm measurements, which were recorded at higher extraction voltages, the I^+ and I^{3+} peaks are each accompanied by a smaller artefact peak at slightly smaller m/q (corresponding to shorter flight times), labelled “reflection”. These peaks appear when the drift tube on the ion side of the spectrometer is at a more negative voltage than the front of the MCP. Consequently, the secondary electrons that are created by ion impact on the mesh that terminates the drift tube are accelerated towards the MCP. These are detected at slightly shorter flight times than the corresponding ions. At the intensity of the FEL used in this work, both single- and multi-photon effects are present in the FLASH data for unaligned 2,6-DFIB. The single-photon contribution is identified by comparison to ALS synchrotron ToF data provided by Ablikim *et al.* [291], for unaligned 2,6-DFIB at the same photon energy, as shown in Figure 7.3. The large contribution from the I^{2+} and I^{3+} fragments in the FLASH spectrum is a clear indication of strong multi-photon processes since only a small amount of I^{2+} ions and no I^{3+} ions exist in the ALS synchrotron data [291]. The generation of F^+ ions is also

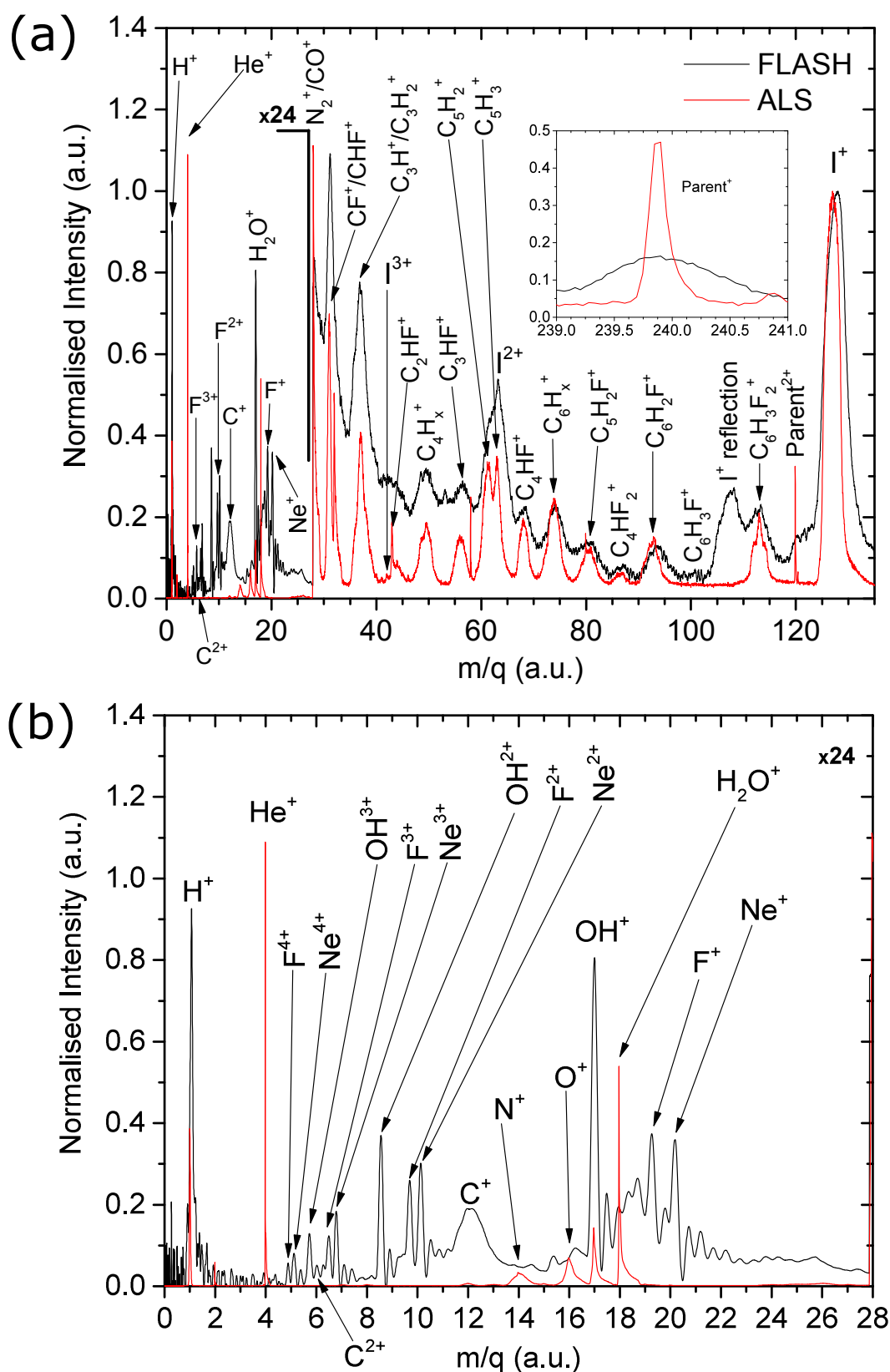


Figure 7.3: Time-of-flight spectra of ions formed after photoionization of unaligned 2,6-difluoriodobenzene in the single- and multi-photon regimes at ALS (black solid line) and FLASH (red solid line), respectively, for (a) the entire and (b) low mass-to-charge range. Both spectra were recorded with high-resolution direct-readout from the MCPs. Assignments for each peak are shown in the figure. The intensity of fragments with m/q below 22 were scaled by a factor of 24. The inset in (a) shows the ToF trace for the parent ion, $C_6H_3F_2I^+$.

due to multi-photon processes at 107 eV, since only a very small amount is generated with synchrotron radiation, whereas multiply charged fluorine fragments up to F^{4+} are observed in the FLASH spectrum. The production of C^+ ions also appears to be a strongly multi-photon process as it has a large (very small) contribution in the FLASH (ALS) spectrum.

7.3.2 Laser-Induced Alignment of DFIB

In this section, the different charged fragments resulting from the Coulomb explosion of adiabatically aligned DFIB molecules were simultaneously recorded with the PImMS1 camera. A set of data were recorded for the strong-field ionization of 2,6-DFIB molecules, while a separate set of data were recorded for the inner-shell ionization of the same molecules.

Figure 7.4 shows the ion images for F^+ , I^+ , I^{2+} , and I^{3+} following the ionization of DFIB using either NIR or XUV photons, with and without adiabatic alignment of molecules. The iodine ions show the most distinct effect from the alignment of DFIB molecules; the distribution is isotropic when the molecules are unaligned but shows two highly localized maxima along the polarization direction of the Nd:YAG pulse when the molecules are aligned. In the latter, the laser field interacts with the molecule by aligning the most polarizable axis (MPA) in the DFIB molecule, which lies along the carbon-iodine bond, parallel to the polarization axis of the laser field. The degree of alignment from these images is quantified by calculating the expectation value $\langle \cos^2 \theta_{2D} \rangle$, where θ_{2D} is the angle between the projection of the recoil velocity of the ion on the detector plane and the polarization axis of the alignment pulse. A $\langle \cos^2 \theta_{2D} \rangle$ value of 0.5 corresponds to an isotropic angular distribution, whilst a $\langle \cos^2 \theta_{2D} \rangle = 1$ corresponds to all molecules being aligned parallel to the polarization axis of the alignment pulse. The $\langle \cos^2 \theta_{2D} \rangle$ values for the relevant ion images in Figure 7.4 are shown in Table 7.2.

A degree of alignment of up to $\langle \cos^2 \theta_{2D} \rangle = 0.97$ is observed using horizontal polarized NIR probe pulses, and 0.94 for horizontally polarized XUV probe pulses. These values are in good agreement with those reported previously by Nevo *et al.* who ob-

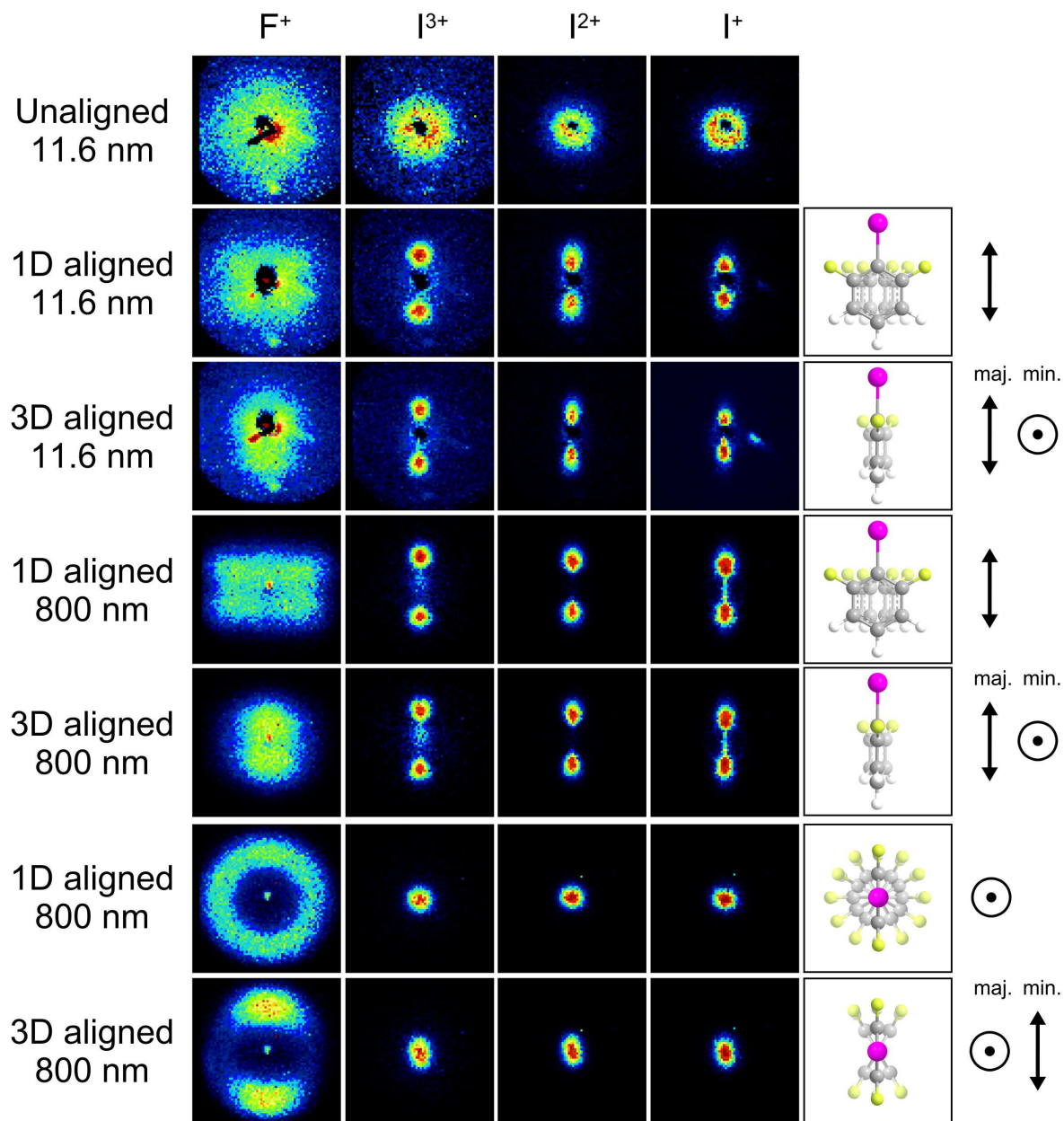


Figure 7.4: Two-dimensional momentum distributions for F^+ , I^{3+} , I^{2+} , and I^+ ions following the ionization of 2,6-difluoroiodobenzene (DFIB) using either 11.6 nm or 800 nm photons recorded with the PImMS1 camera. Background images recorded with the molecular beam switched off were subtracted. The first row of images was recorded without the adiabatic alignment field. For the subsequent rows, the direction of the (major and minor) polarization axes of the Nd:YAG pulse is sketched on the right. Note that the images with 11.6 nm and 800 nm were taken with different spectrometer voltages (see text). The radial range corresponding to the outermost kinetic energy release channel was used to determine the value of $\langle \cos^2 \theta_{2D} \rangle$.

	F ⁺	I ³⁺	I ²⁺	I ⁺
Unaligned, 11.6 nm	0.50	0.49	0.49	0.40
1D aligned, 11.6 nm	0.47	0.90	0.91	0.89
3D aligned, 11.6 nm	0.55	0.90	0.94	0.94
1D aligned, 800 nm	0.39	0.95	0.96	0.95
3D aligned, 800 nm	0.58	0.94	0.97	0.96

Table 7.2: The $\langle \cos^2 \theta_{2D} \rangle$ values directly extracted from the 2D momentum distributions shown in Figure 7.4 using the method described in Reference [159]. The radial range corresponding to the outermost kinetic energy release channel was used to determine the value of $\langle \cos^2 \theta_{2D} \rangle$. The polarization of the Nd:YAG alignment and NIR/XUV probe pulses were both set parallel to the detector plane.

served $\langle \cos^2 \theta_{2D} \rangle$ values of up to 0.96 [158] in the adiabatic 1D-aligned of 2,6-DFIB. In the same work, the authors also showed that the degree of alignment reduced to 0.94 in the absence of the deflector [158]. A degree of alignment of $\langle \cos^2 \theta_{2D} \rangle = 0.93$ was also observed for 1D-aligned 3,5-DFIB by Viftrup *et al.* using a nanosecond Nd:YAG alignment pulse [306]. The relatively high $\langle \cos^2 \theta_{2D} \rangle$ values for the iodine fragments suggests that alignment can be probed with high fidelity using both NIR and XUV pulses. It also shows that the axial recoil approximation [64, 229] is valid in both cases since the emission direction of the iodine ions reflects the direction of the iodine-carbon axis at the moment the initial ionization occurs. Although the slightly larger $\langle \cos^2 \theta_{2D} \rangle$ values from the NIR ion images suggest that a higher degree of alignment was achieved with the NIR than with the XUV pulse, this is in fact not the case since the NIR data contains contributions from “geometric alignment” effects that leads to an overestimation of $\langle \cos^2 \theta_{2D} \rangle$ values in the NIR case.

Geometric alignment effects appear in the NIR case as the polarization direction of the NIR pulses were set parallel to the YAG pulse, which leads to the enhanced ionization and fragmentation probability for molecules that have their C-I axis parallel to the polarization direction of the NIR probe pulse. In the XUV case, probing via (non-resonant) inner-shell ionization with the XUV pulse polarized parallel to the alignment pulse leads to isotropic ion images, as shown in Figure 7.4, which has been previously reported by Küpper *et al.* [271]. This shows that the ionization probability is almost isotropic with the XUV pulse, in contrast to the NIR pulse. To avoid geo-

metric alignment (or probe) effects with the NIR pulse, the polarization direction of the NIR probe pulse is usually set perpendicular to the alignment pulse [158].

Figure 7.5 shows the ion images for the cases corresponding to with ($\parallel / \parallel$) and without ($\parallel / \perp$) the presence of geometric alignment where the NIR probe laser was polarized either parallel or perpendicular to the alignment laser, respectively. It should be noted that the major component of the alignment laser pulse was parallel ($\parallel$) to the detector for all data presented in this figure. The $\langle \cos^2 \theta_{2D} \rangle$ values for the ion images presented in Figure 7.5 are shown in Table 7.3. Although slightly smaller $\langle \cos^2 \theta_{2D} \rangle$ values were extracted for data without geometric alignment effects, a relatively high degree of alignment of up to 0.93 was still achieved. The $\langle \cos^2 \theta_{2D} \rangle$ value for I^{3+}

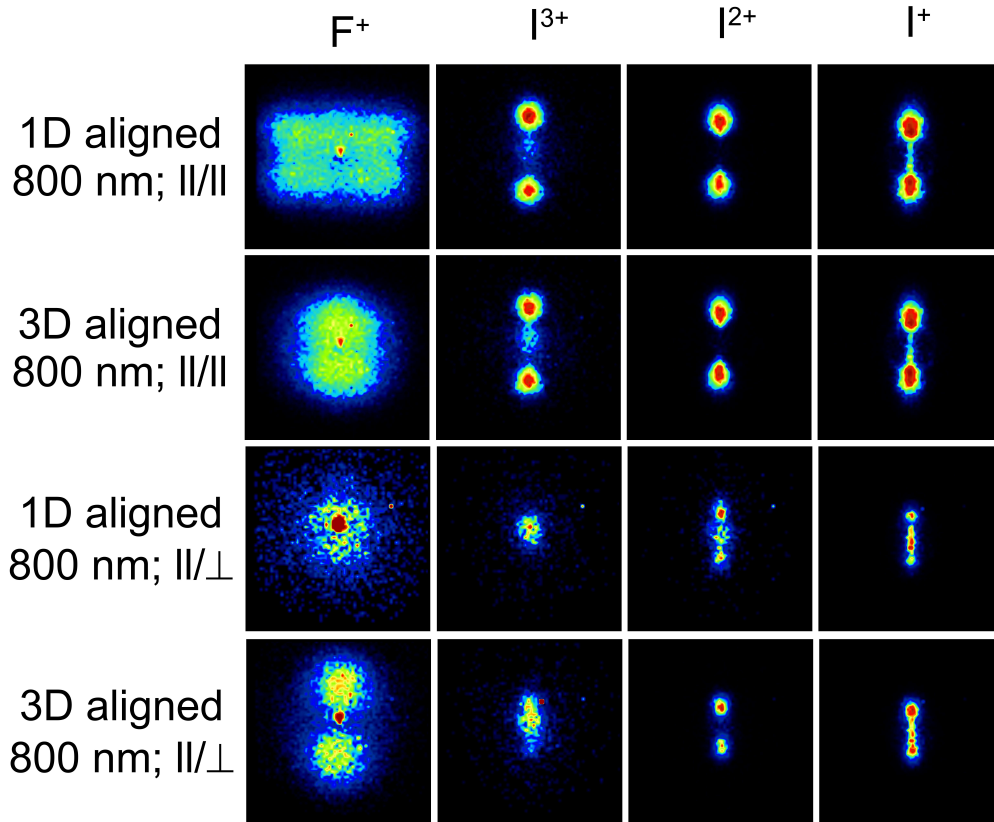


Figure 7.5: Two-dimensional momentum distributions for F^+ , I^{3+} , I^{2+} , and I^+ ions with ($\parallel / \parallel$) and without ($\parallel / \perp$) geometric alignment effects where. The label (X/Y) in the figure corresponds to the polarization of the Nd:YAG alignment and NIR probe pulses being set to X and Y, respectively. These ion fragments were generated from the ionization of laser-aligned 2,6-difluoroiodobenzene (DFIB) using 800 nm photons recorded with the PImMS1 camera. Background images recorded with the molecular beam switched off are subtracted. Note that the images with 11.6 nm and 800 nm were taken with different spectrometer voltages. The radial range corresponding to the outermost kinetic energy release channel was used to determine the value of $\langle \cos^2 \theta_{2D} \rangle$.

	F ⁺	I ³⁺	I ²⁺	I ⁺
1D aligned, 800 nm;	0.39	0.95	0.96	0.95
3D aligned, 800 nm;	0.58	0.94	0.97	0.96
1D aligned, 800 nm; ⊥	N/A	N/A	0.89	0.93
3D aligned, 800 nm; ⊥	0.72	N/A	0.93	0.93

Table 7.3: The $\langle \cos^2 \theta_{2D} \rangle$ values extracted from the 2D momentum distributions with and without geometric alignment effects for images in Figure 7.5 using the method described in Reference [159]. The radial range corresponding to the outermost kinetic energy release channel was used to determine the value of $\langle \cos^2 \theta_{2D} \rangle$. The polarization of the Nd:YAG alignment pulse was set to parallel (to the detector plane) in all four cases, while the polarization of the NIR probe pulse was set to either parallel (||) or perpendicular (⊥) as indicated in the table.

ions in the perpendicular case could not be extracted as there were very few I³⁺ ions generated. This occurs due to the weaker interaction between the molecule and the perpendicularly polarized probe pulse that ultimately lead to a molecular ion that was not highly charged enough to generate I³⁺ ions.

The F⁺ ion images contain information about the alignment of the molecular plane in space, as has been previously reported for the DFIB molecule by several authors [158, 306, 307]. In 1D alignment of molecules using linearly polarized Nd:YAG pulses, molecules can freely rotate around their MPA (the carbon-iodine axis); this leads to the emission of F⁺ ions as two torus-shaped distributions around the polarization axis of the alignment pulse. The distribution of ions are then projected onto the 2D detector as either two thick lines or as a ring, depending on the direction of the polarization axis of the alignment pulse with respect to the detector.

In Figure 7.4, these features are clearly visible in the images recorded with the NIR probe pulse, while the same, slightly less pronounced features also exist in the images taken with the XUV probe pulse. It should be noted that the spectrometer voltages were a factor of two higher when recording the images with the XUV probe pulse, which causes the features in the ion images to become more compressed than for the NIR case. The dark central spot present in the images recorded with the XUV pulse is due to the saturation of the corresponding PImMS1 pixels by Ne⁺, Ne²⁺, Ne³⁺ and H₂O⁺ ions, which all possess low kinetic energies. As discussed in Section 7.3.1, significantly more neon and water ions are generated with the XUV pulses than with

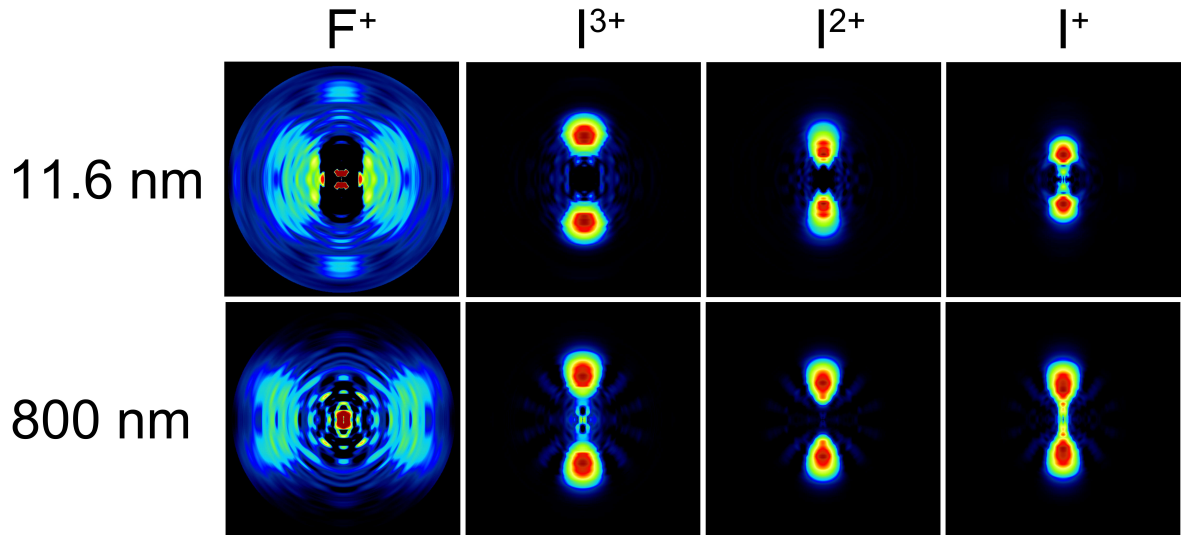


Figure 7.6: pBasex-inverted ion images for F^+ , I^{3+} , I^{2+} , I^+ ions are (from left to right) shown following the ionization of 1D-aligned 2,6-difluoriodobenzene using either 11.6 nm (top) or 800 nm (bottom) photons recorded with the PImMS1 camera. Note that the images with 11.6 nm and 800 nm were taken at different spectrometer voltages.

the NIR pulses.

The ion images of 1D-aligned DFIB in Figure 7.4 were inverted using the pBasex package [213] which returns an image corresponding to an infinitesimally thin slice through the centre of the reconstructed 3D distribution of ions, as shown in Figure 7.6. The corresponding $\langle \cos^2 \theta_{2D} \rangle$ values are shown in Table 7.4. Following pBasex-inversion, slightly higher $\langle \cos^2 \theta_{2D} \rangle$ values are observed for iodine fragments in the 11.6 nm case when compared to the corresponding raw data. The higher values reflect the improved signal:noise in the pBasex images when compared to the raw data. While approximately the same values were generated in the 800 nm case, which reflect the fact that no significant improvement in signal:noise is seen between the pBasex and raw 800 nm data. A significant reduction in the $\langle \cos^2 \theta_{2D} \rangle$ value is observed in the F^+ pBasex-

	F^+	I^{3+}	I^{2+}	I^+
1D aligned, 11.6 nm;	0.41	0.92	0.93	0.92
1D aligned, 800 nm;	0.25	0.94	0.95	0.94

Table 7.4: The $\langle \cos^2 \theta_{2D} \rangle$ values extracted from the 2D momentum distributions for pBasex-inverted images in Figure 7.6 using the method described in Reference [159]. The radial range corresponding to the outermost kinetic energy release channel was used to determine the value of $\langle \cos^2 \theta_{2D} \rangle$. The polarization of the Nd:YAG alignment and NIR probe pulses were set parallel to the detector plane in both cases.

inverted image at 800 nm. This reflects the emission of the fluorines perpendicular to the C-I axis (but in the plane of the detector) which as a result leads to a $\langle \cos^2 \theta_{2D} \rangle$ value that is significantly smaller than 0.5 (isotropic). In the 11.6 nm case, a small decrease is also observed in the pBasex-inverted F^+ data, although the signal:noise in this pBasex data is still worse than the corresponding 800 nm data.

In 3D alignment of molecules, an elliptically polarized Nd:YAG pulse was used with an ellipticity intensity ratio of 2.2:1.0. The major and minor axes of polarization interact with the most and second most polarizable axes of DFIB, respectively, such that the carbon-iodine axis aligns with the major polarization axis of the elliptical field and the molecular plane aligns to the minor polarization axis. The resulting F^+ ions are more tightly confined than in the case of 1D alignment, as evident in their corresponding 2D detector images shown in Figure 7.4. If the polarization of the NIR probe pulse is perpendicular instead of parallel to the polarization axis of the alignment pulse, then molecules will be free of any geometric alignment effects. In the case of 3D aligned molecules with the polarization axis of the alignment pulse perpendicular to the NIR probe pulse (last row of Figure 7.5), the presence of geometric alignment leads to a more anisotropic distribution of F^+ ions and a much higher $\langle \cos^2 \theta_{2D} \rangle$ value of 0.72.

If instead, the major axis of the elliptical polarization is orient perpendicular to the ion detector (and to the polarization of the NIR probe pulse), then an “end view” of the molecule is obtained (rows 3 and 4 in Figure 7.5). In the case of 1D alignment (second last row of Figure 7.4), the I^{n+} ions are strongly confined to a central spot, while the F^+ ions are projected onto a ring since the molecular plane is free to rotate around the MPA (carbon-iodine axis). In the case of 3D alignment (last row of Figure 7.4), the F^+ ions are strongly localized along the minor axis of polarization, indicating that the molecular plane is now confined to the minor polarization plane of the alignment pulse.

Since the PImMS1 camera can record all ions simultaneously under the same experimental conditions, it should in principle be possible to find angular covariances that show correlation between the iodine and fluorine fragments, as demonstrated in

the work of Slater *et al.* [56]. However, no such covariances were found in the data presented in this chapter due to the very low ion detector voltages that were unfortunately used in the measurements presented in this chapter, which makes the detection of two or more correlated ions near-impossible. As mentioned earlier, low ion detector voltages were used to overcome the overlapping of ion clusters in the ion detector images that were present due to the relatively high count rate used in the experiment to ensure good signal:noise in the photoelectron images. In future FEL measurements that use optimum voltages on the ion detector, shot-to-shot variations in the FEL pulse will lead to the masking of correlations between two or more ions as was shown by Frasinski *et al.* and Kornilov *et al.* [309, 310]. Frasinski *et al.* corrected their FEL data for shot-to-shot fluctuations in the FEL pulse using the method of partial covariance method [309] which revealed competing ionization processes in neon atoms at 1062 eV [309].

7.3.3 Kinetic Energy Distributions of DFIB

In this section, the Coulomb explosion process is investigated by analysing the kinetic energy distribution of fragment ions that were generated by either multi-photon inner-shell ionization with an XUV pulse or strong-field ionization with an NIR pulse. Figure 7.7 shows the resulting kinetic energy distributions for the iodine fragments. A clear increase in the ion kinetic energy release is seen with increasing ion charge.

At the given FEL and NIR-laser intensities and pulse lengths, several similarities and differences appear in the kinetic energy distributions for strong-field ionization with 800 nm and for inner-shell multi-photon ionization with 11.6 nm. In the case of I^+ , similar kinetic energy distributions are generated with both 800 nm and 11.6 nm, which suggests that the generation of I^+ is independent of the details of the ionization process. By applying Gaussian fits to the kinetic energy distributions, the individual components in the distribution can be identified and the average kinetic energies that the fragment is ejected with can be determined from the mean of the Gaussian distribution. The resulting Gaussian fits to the I^+ distributions is shown in Figure 7.8, and the corresponding mean KER values for each component are listed in Table 7.5.

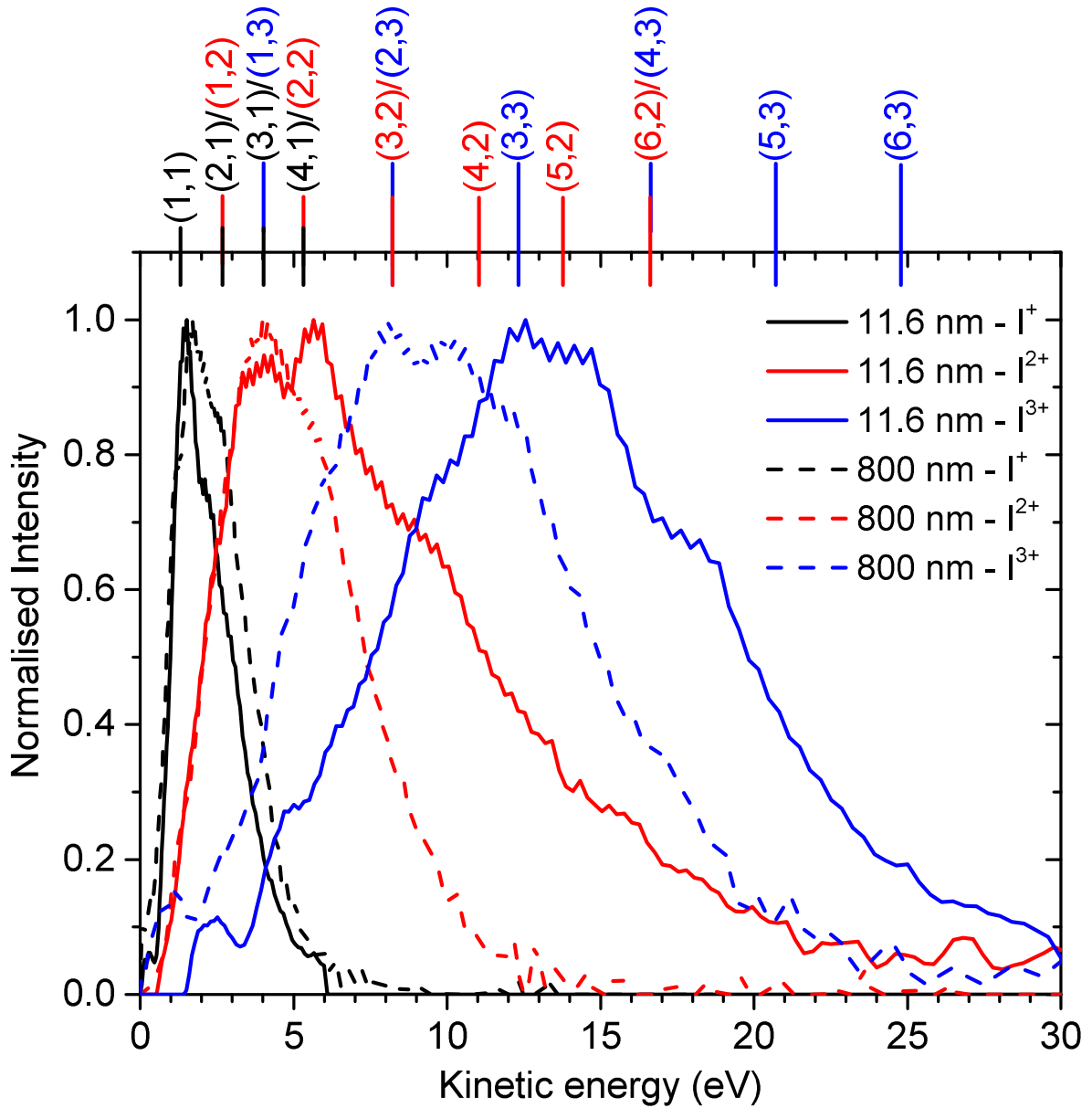


Figure 7.7: Kinetic energy distributions of I^+ (black), I^{2+} (red) and I^{3+} (blue) ions extracted from their corresponding pBasex-inverted ion images for both multi-photon inner-shell ionization using an XUV pulse (solid lines) and strong-field ionization using an NIR pulse (dashed lines). Each distribution was normalized to the maximum intensity of its corresponding distribution. The vertical lines at the top of the figure indicate the expected kinetic energy of the I^+ (black), I^{2+} (red), and I^{3+} (blue) ions assuming pure Coulombic repulsion from a singly, doubly, triply, etc. charged co-fragment (see text). They are labelled (n, m) , where n is the charge of the iodine ion and m the charge of the co-fragment.

	I	II	III	IV
I^+ - 11.6 nm	1.42(1)	2.50(2)	-	-
I^+ - 800 nm	1.48(1)	2.70(6)	-	-
I^{2+} - 11.6 nm	2.92(11)	5.24(16)	8.65(63)	14.20(186)
I^{2+} - 800 nm	3.47(5)	6.02(26)	-	-
I^{3+} - 11.6 nm	13.21(21)	21.93(303)	-	-
I^{3+} - 800 nm	7.63(12)	11.75(46)	-	-

Table 7.5: The mean value of the individual Gaussian fits applied to the experimental kinetic energy distributions in eV. The KER values are shown for up to four individual Gaussian fits (I-IV). The fitting error of the mean value is shown in brackets.

In both NIR (grey line) and XUV (black line) cases, the I^+ ion is ejected with an average energy of approximately 1.4 and 2.6 eV. Furthermore, these kinetic energies compare well with those determined by an electron-ion-ion coincidence experiment performed with synchrotron radiation at the same photon energy by Rolles and coworkers [291], where a maximum in the I^+ kinetic energy distribution was observed at ~ 1.4 eV

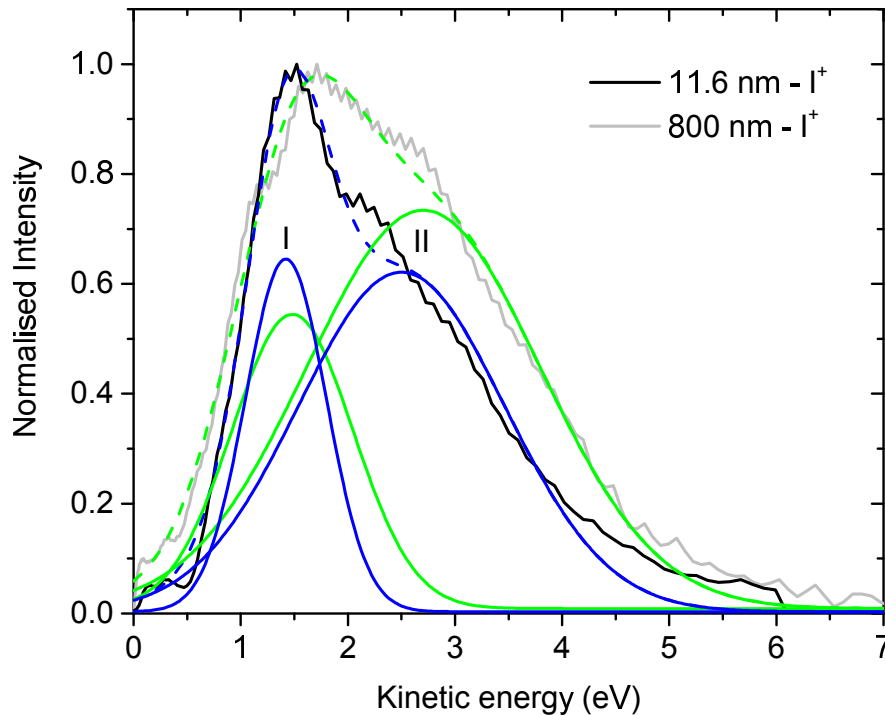


Figure 7.8: Kinetic energy distributions from pBasex-inverted ion images for I^+ ions following the ionization of DFIB with either 11.6 nm (black solid line) or 800 nm (grey solid line) photons. Gaussian fits to each distribution with the individual components (blue and green solid lines) and their sum (blue and green dashed lines) are shown. Both experimental distributions were normalized to the maximum intensity of their corresponding distribution. The individual components contributing to the overall distributions are labelled as I and II.

for I^+ ions coincident with a singly charged co-fragment (DFB^+) and ~ 2.8 eV for I^+ ions coincident with a doubly charged co-fragment (DFB^{2+}) [291]. It should be noted that the authors assumed a two-body break-up mechanism. The latter is exactly double the former; both suggest that the equilibrium distance, r_0 , between the two fragments (with charges of q_1 and q_2) is 491 pm as given by

$$E = \frac{k q_1 q_2}{r_0} \quad (7.1)$$

where k is the electrostatic force constant. If the charge on one of the fragments is increased by a given factor, then from Equation (7.1) the resulting kinetic energy release in the fragments should increase by the same factor. Therefore, the charge of the co-fragment, DFB, that the iodine fragment is partnered with can be tentatively inferred by comparison to Table 7.6 which lists the expected KER of iodine fragments partnered with varying charge states of DFB at a fixed equilibrium separation of 491 pm [291]. The good agreement between the I^+ kinetic energies from this work (XUV: 1.42 eV and 2.50 eV; NIR: 1.48 eV and 2.70 eV) with those in Table 7.6 (1.38 eV and 2.77 eV) indicate that I^+ ions are ejected with either DFB^+ or DFB^{2+} co-fragments in both the XUV and NIR cases.

The individual Gaussian fits applied to the kinetic energy distributions of I^{2+} ions are shown in Figure 7.9(a). In the NIR case, I^{2+} ions are ejected with either DFB^+ or DFB^{2+} co-fragments upon comparison to Table 7.6. In the XUV case, two additional components contribute to the high kinetic energy side of the distribution. Thus, by comparison to Table 7.6, the four components (features I-IV) are shown to correspond to I^{2+} ions partnered with either DFB^+ , DFB^{2+} , DFB^{3+} , or DFB^{5+} co-fragments.

	DFB^+	DFB^{2+}	DFB^{3+}	DFB^{4+}	DFB^{5+}	DFB^{6+}
I^+	1.38	2.77	4.15	5.53	6.92	8.30
I^{2+}	2.77	5.53	8.30	11.07	13.84	16.60
I^{3+}	4.15	8.30	12.45	16.70	20.75	24.90

Table 7.6: The calculated kinetic energy release of iodine fragments partnered with various charge states of the DFB co-fragment (in eV) at a fixed equilibrium distance of 491 pm [291].

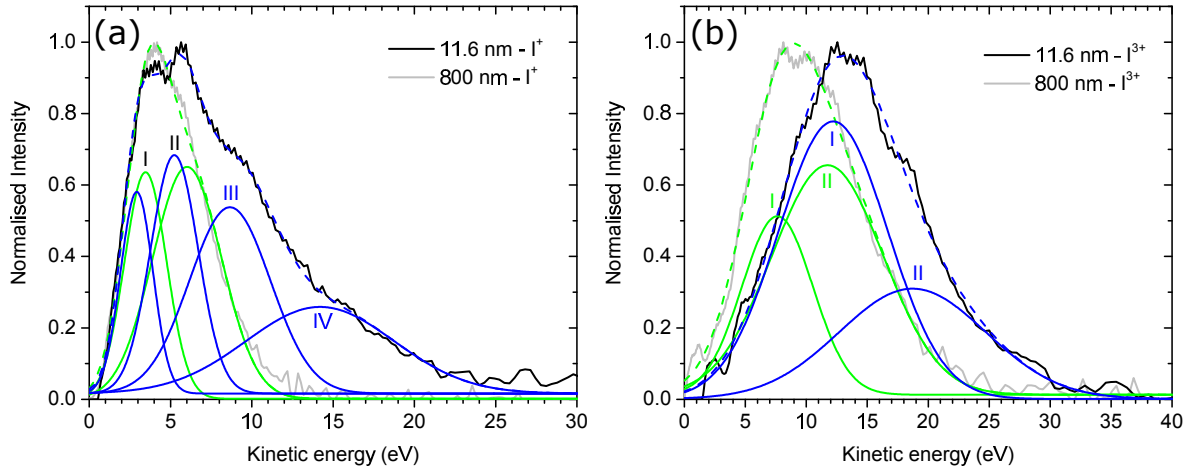


Figure 7.9: Kinetic energy distributions from pBasex-inverted ion images for (a) I^{2+} and (b) I^{3+} ions following the ionization of DFIB with either 11.6 nm (black solid line) or 800 nm (grey solid line) photons. Gaussian fits to each distribution with the individual components (blue and green solid lines) and the sum of these components (blue and green dashed lines) are shown. Both experimental distributions were normalized to the maximum intensity of their corresponding distribution. The individual components contributing to the overall distributions are labelled as I, II, III and IV, where applicable.

The kinetic energy distribution for I^{3+} ions generated by an XUV pulse appear at higher energies than the corresponding distribution for NIR, as shown in Figure 7.9(b). In the latter, I^{3+} ions are ejected with either DFB^{2+} or DFB^{3+} ions, while the former generates I^{3+} ions with either DFB^{3+} or DFB^{5+} ions. The typical kinetic energies that iodine and fluorine fragments are ejected with are given by the expectation value of their kinetic energy release, as shown in Table 7.7.

The higher kinetic energies observed in the I^{2+} and I^{3+} fragments generated by an XUV pulse confirm the above finding that a higher overall degree of ionization is achieved through multi-photon inner-shell ionization than with strong-field ionization at these intensities and pulse durations. Higher kinetic energies are also observed for

	F^+	I^{3+}	I^{2+}	I^+
800 nm	8.1	9.5	4.8	2.2
11.6 nm	10.0	13.7	8.1	2.1

Table 7.7: The expectation value of the kinetic energy, $\langle \text{KE} \rangle$, with which the F^+ , I^{3+} , I^{2+} , and I^+ ions are ejected with (in eV) following the Coulomb explosion of 1D-aligned DFIB molecules with either 11.6 nm or 800 nm photons. The $\langle \text{KE} \rangle$ was extracted from the pBasex-inverted ion images shown in Figure 7.7.

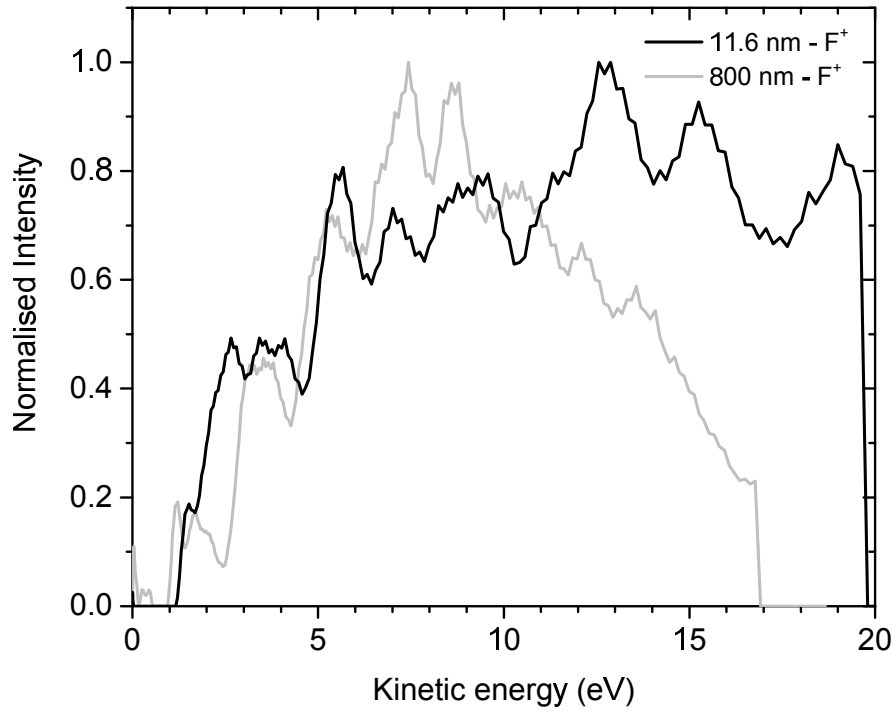


Figure 7.10: Kinetic energy distribution of F^+ ions were extracted from their corresponding pBasex-inverted ion images for multi-photon inner-shell ionization by an XUV pulse (black line) and strong-field ionization by an NIR pulse (grey line). Each distribution was normalized to the maximum intensity of its corresponding distribution.

F^+ ions generated through inner-shell ionization (black line) than through strong-field ionization (grey line), as shown in Figure 7.10.

In summary, the resulting kinetic energies of I^+ ions are the same in both multi-photon inner-shell ionization and strong-field ionization, while I^{2+} , I^{3+} , and F^+ ions are generated with higher kinetic energies from the former due to the higher degree of ionization with the XUV pulse than with the NIR pulse.

7.3.4 Mixed-Field Orientation of DFIB

In the previous sections, the ion images generated from aligned molecules contained an up-down symmetry. In those measurements, the YAG alignment pulse was polarized parallel to the detector, leading to an angle between the static electric extraction field from the ion optic plates, E_{stat} , and the AC field of the YAG pulse, E_{YAG} , of $\beta = 90^\circ$. As the Coulomb explosion pulse was also polarized parallel to the detector, equal numbers of molecules were probed that were facing upwards and downwards. A sketch of the angle β that relates E_{stat} and E_{YAG} to each other relative to E_{pulse} and the

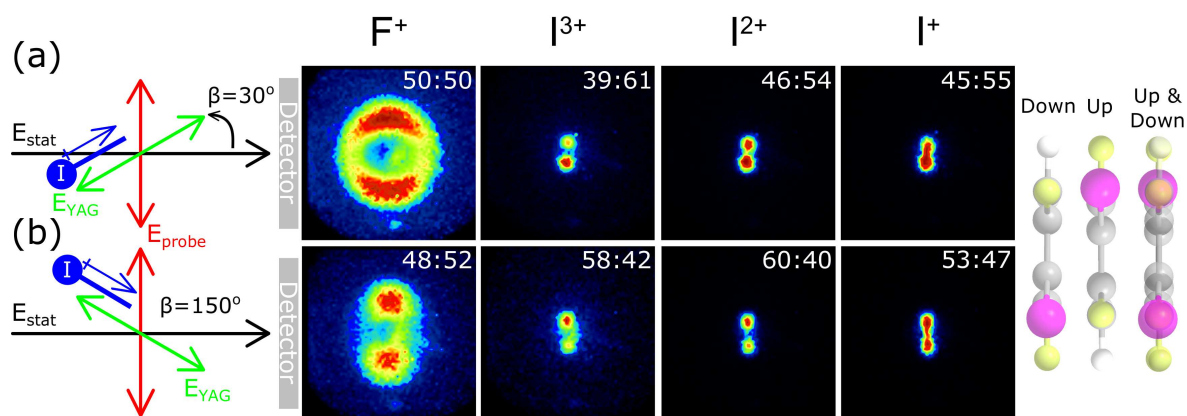


Figure 7.11: F^+ , I^{3+} , I^{2+} , and I^+ ion images after the Coulomb explosion of oriented and aligned 2,6-difluoroiodobenzene molecules using 800 nm photons. In (a), the molecules were 1D-aligned and oriented with the I-end downwards using a linearly polarized light that was rotated away from the detector plane by an angle of $\beta = 30^\circ$. In (b), the molecules were 3D-aligned and oriented with the I-end upwards using elliptically polarized light that was rotated away from the detector plane by an angle of $\beta = 150^\circ$. The annotated insets on the left hand side show the polarization axis of the probe (red), of the YAG alignment pulse (green), and the direction of the static electric field (black). The direction that the molecule and its permanent dipole moment face in both cases are shown in blue. The asymmetry ratios are indicated in the top right corner of the ion images. A sketch of oriented 3D-aligned 2,6-DFIB molecules is also shown on the right hand side.

detector plane is shown in Figure 7.11.

This symmetry can be broken in order to preferentially orient the molecule in a particular direction, by rotating E_{YAG} away from the detector such that $\beta \neq 90^\circ$. The permanent dipole moment (2.25 D [158]) in DFIB points away from the iodine (negative) end of the molecule towards the phenyl ring (positive) end, since the most polarizable part of the molecule is located across the carbon-iodine bond. Therefore, the iodine end of the molecule is positioned towards the repeller plate as the permanent dipole moment orients parallel to the electric field. The iodine ions can be preferentially eject downwards (upwards) if $\beta < 90^\circ$ ($\beta > 90^\circ$).

In a proof-of-principle experiment, all fragments from DFIB molecules that were both aligned and oriented were recorded simultaneously with the PImMS1 camera, the most significant of those fragments are presented in Figure 7.11. In panel (a), DFIB was 1D aligned using a linear polarized Nd:YAG pulse that was rotated by $\beta = 30^\circ$ away from the detector, leading to more iodine ions ejected in the ‘downward’ direction. In panel (b), DFIB was 3D aligned using an elliptically polarized YAG pulse with it’s

major component rotated by $\beta = 150^\circ$, leading to more iodine ions ejected in the ‘upward’ direction.

The degree of orientation is quantified by integrating the counts in the upper and lower halves of the detector image to obtain the corresponding asymmetry ratios, $I_{\text{up}}/(I_{\text{up}} + I_{\text{down}}) : I_{\text{down}}/(I_{\text{up}} + I_{\text{down}})$, as shown in the top right corner of the images. Although asymmetry ratios of approximately 60:40 are observed in this geometry, these were not as high as the 67:33 ratio achieved by Nevo *et al.* with adiabatically aligned 2,6-DFIB molecules [158]. In the I^+ images, the asymmetry ratios are slightly lower due to saturation of the central pixels in those images.

The timing resolution in the present experiment was not sufficient to detect orientation effects in the ToF spectrum, which have been observed by Nevo *et al.* in the splitting of the I^{n+} peak into “forward” and “backward” components corresponding to the ions emitted towards or away from the ion detector [158]. The F^+ ion distributions do not show any significant orientation effects. Although this is puzzling at first, the up-down asymmetry in the F^+ ions is in fact hidden in this geometry when compared to the alignment-only ion images which had an “end-view” of the molecule that used a vertically polarized Nd:YAG pulse. The hidden orientation effects in this geometry is illustrated by sketches on the right hand side of Figure 7.11.

7.4 Conclusions

In summary, a high degree of 1D and 3D alignment was achieved using adiabatic Nd:YAG pulses. Relatively modest orientation effects were also observed through the mixed-field orientation of aligned DFIB molecules. In both cases, a deflector was used to select DFIB molecules in their lowest rotational quantum states, which has been previously shown by Nevo *et al.* to improve the degree of alignment and orientation with deflection than without [158].

Alignment and orientation of molecules was probed with high fidelity using the NIR and XUV probe pulses since they both induced similar Coulomb explosion processes despite the very different ionization mechanisms induced by the two pulses. In the NIR

case, valence electrons are sequentially removed from the molecule through strong-field ionization. While in the XUV case, inner-shell ionization of molecules proceeds via a sequence of inner-shell ionizations quickly followed by Auger decay.

A degree of alignment of up to $\langle \cos^2 \theta_{2D} \rangle = 0.97$ were observed for horizontally polarized (*i.e.* parallel to the detector plane) NIR probe pulses, 0.93 for vertically polarized (*i.e.* perpendicular to the detector plane) NIR probe pulses, and 0.94 for horizontally polarized XUV probe pulses. In all three measurements, the polarization of the Nd:YAG alignment pulses was horizontal. These values are in good agreement with the value of 0.96 reported by Nevo *et al.* for 1D-aligned 2,6-DFIB who used vertically polarized NIR probe pulses that were perpendicular to the polarization axis of the nanosecond Nd:YAG alignment pulse to avoid “geometric alignment” effects, which would be present in the horizontally polarized case. Asymmetry ratios of up to 60:40 were achieved in this work for 1D- and 3D-aligned 2,6-DFIB molecules, whilst a 67:33 ratio was achieved by Nevo *et al.*. In the absence of the Nd:YAG alignment pulse, isotropic ion images were generated by the XUV probe pulse. Thus, non-resonant inner-shell ionization has an isotropic ionization probability and does not possess any geometric alignment effects, which do appear in strong-field ionization using NIR pulses.

In general, the results in this chapter have demonstrated that the Coulomb explosion of 2,6-DFIB is possible through both strong-field ionization and inner-shell ionization, with similar results obtained from both. In the following chapter, the CEI technique using inner-shell ionization is extended to femtosecond-resolved pump-probe studies into the photodissociation and charge transfer dynamics of 1D-aligned CH₃I and 2,6-DFIB molecules using the FLASH FEL as the probe pulse.

Chapter 8

Imaging Dissociation and Charge Transfer Using the FLASH FEL

8.1 Introduction

There are many time-resolved pump-probe techniques that have been employed to study photo-induced reactions in a multitude of systems. Diffraction-based techniques, such as ultrafast electron diffraction [33, 278, 283, 311–316] and X-ray scattering [33, 317], have been employed in pump-probe schemes where an optical pulse initiates a process of interest, and after a set time delay, the incoming beam of electrons or X-rays diffract from the sample. From the resulting diffraction pattern, the structure of the sample can be inferred.

For example, Minitti *et al.* [317] investigated the ring-opening reaction of 1,3-cyclohexadiene to 1,3,5-hexatriene using time-dependent X-ray scattering at the Linac Coherent Light Source (LCLS) free-electron laser facility. They used a femtosecond 267 nm pump pulse to initiate the ring-opening reaction followed by a time-delayed femtosecond hard X-ray pulse which diffracted from the molecule. By recording diffraction patterns at various pump-probe delays, the authors recorded a “molecular movie” of the evolving reaction which showed that 1,3,5-hexatriene was generated after a pump-probe delay of only 30 fs [317].

As mentioned in Chapter 5, a pure form of the sample must be prepared in the interaction region in order to obtain meaningful structural information. In the case of gas-phase reactions, isomers of molecules, such as *trans*- or *cis*-3-fluorophenol [287], may exist in the sample and could distort the structural information that is extracted from the diffraction of the sample [267].

FELs can also be used to obtain structural information of a molecule in the gas-phase using non-diffractive methods such as Coulomb explosion imaging (CEI) [77, 78, 81, 262, 308, 318]. The ultrabright and ultrafast extreme-ultraviolet (XUV) or X-ray optical pulses produced by FELs can induce the inner-shell ionization of a molecule in which at least two electrons are removed from the molecule (see Section 4.3 in Chapter 4). This leads to the Coulomb explosion of the molecule to generate many fragment ions. The velocities of the recoil ions can be recorded, using VMI and position- and time-sensitive detectors, to obtain structural information of the molecule.

In time-limited beamtime experiments, it is desirable to record all charged fragments under the same experimental conditions simultaneously for two reasons. Firstly, to maximize the quality and quantity of structural information that can be obtained under such time-critical conditions. Secondly, to enable a like-for-like comparison between multiple fragments recorded in the same acquisition cycle under the same experimental conditions, which is useful since FELs are unstable light sources (see Section 4.5.3 in Chapter 4). In gas-phase VMI imaging experiments utilizing the FLASH FEL, two detection methods are typically used: a delay line anode detector (DLA) under coincidence conditions (*i.e.* $\ll 1$ count per acquisition cycle) or a CCD camera that is gated over a particular ToF range corresponding to a single mass-to-charge fragment. In both cases, recording all ions of interest from a molecule with good statistics can typically span an entire beamtime, particularly since the FEL pulse can generate many charged fragments due to its high photon energy and intensity.

In the case of DLA detectors, the bunch-train mode of FLASH [319, 320] can be used to raise the repetition rate of the FLASH FEL from 10 Hz to 100–800 Hz in order to record data with sufficient statistics under coincidence conditions. Although the in-house burst-mode optical parametric amplified laser can match the pulse pattern

of the FLASH multi-bunch mode, it generates rather low pulse energies in the μJ range. Consequently, it is very difficult to use the high repetition rate burst-mode laser pulses in pump-probe experiments on dilute gas-phase targets, which require much higher pulse energies. To carry out such pump-probe experiments, the in-house FLASH pump-probe Ti:Sapphire laser is used which can generate pulse energies on the order of mJ, but this comes at the cost of the repetition rate of the experiment being limited to 10 Hz. Thus, it is not ideal to use DLA detectors at 10 Hz for pump-probe experiments on dilute gas-phase target molecules.

In the case of a CCD camera set-up, the time-gating requirement of the camera means that only a single mass-to-charge fragment can be recorded in each individual data set. The inherent instability of the FEL source in laser timing, pointer position and output intensity can lead to inconsistencies between different ions measured in separate CCD camera data sets, making it difficult to compare individual mass-to-charge fragments arising from the same system. With the PImMS1 camera, these limitations can be overcome, since all ions can be recorded simultaneously under identical experimental conditions. This not only reduces the acquisition time, but also substantially simplifies the data analysis procedure.

In this chapter, the PImMS1 camera was utilized in a series of time-resolved UV laser-pump XUV FEL-probe experiments on CH_3I and 2,6-difluoriodobenzene (DFIB) at the free-electron laser in Hamburg (FLASH). The femtosecond UV pulse ($267 \pm 2.5 \text{ nm}$) initiates the photodissociation of the carbon-iodine bond in the target molecules of methyl iodide (CH_3I) and 2,6-difluoriodobenzene (DFIB, $\text{C}_6\text{H}_3\text{F}_2\text{I}$). At a series of fixed delays following the “pump” pulse, the resulting fragments were ionized and Coulomb exploded with an intense, femtosecond XUV ($11.6 \pm 0.56 \text{ nm}$; 107 eV) pulse from the FLASH free-electron laser (FEL). The photodissociation of CH_3I and DFIB have been discussed in detail previously in Chapter 1. The FEL was tuned to the photon energy of 107 eV at which the iodine 4d shell is energetically accessible and has a relatively large partial absorption cross-section for photoionization ($\sim 3.8 \text{ Mb}$ [240]). Both these points make it likely that an inner-shell electron from the 4d orbital of iodine can be ejected after absorption of a 107 eV photon by the molecule. The core

vacancy is then filled by a fast Auger decay to generate a doubly or triply charged cationic fragment [291]. The multiply charged molecular ion then Coulomb explodes to generate several recoil ions. The majority of data presented in this chapter was recorded with the PImMS1 camera, but a limited data set recorded with a conventional CCD camera is presented for comparison. To account for fluctuations in the FEL's pulse energy and arrival-time, corrections were applied to the data from both types of cameras.

8.2 Experimental Methods

8.2.1 Experiment in Brief

The experimental equipment and parameters used in this chapter are very similar to those described in Section 7.2 of the previous chapter, with only a brief summary and the crucial differences discussed in this section. A molecular beam containing either methyl iodide or 2,6-difluoroiodobenzene seeded in neon (total gas mixture pressure of 20 bar) was intersected by three laser pulses: a 1064 nm adiabatic alignment pulse, a 267 nm pump pulse, and an 11.6 nm probe pulse.

The 1064 nm adiabatic alignment pulse ($\tau = 12$ ns (FWHM); $I_0 = 8 \times 10^{11}$ W cm $^{-2}$) was generated with a Nd:YAG nanosecond laser. The 267 nm pump pulse ($\tau = 150 \pm 50$ fs (FWHM); $I_0 = 7 \times 10^{12}$ W cm $^{-2}$) was generated from the frequency-tripled output of the 800 nm beam that originated from the in-house Ti:Sa 10 Hz laser system at FLASH. The 11.6 nm probe pulse ($\tau = 100$ fs (FWHM); $I_0 = 3 \times 10^{13}$ W cm $^{-2}$) was generated by the FLASH free-electron laser. The focus of the UV pump pulse ($\sim 40 \mu\text{m}$) was chosen to be much larger than that of the FEL ($\sim 20 \mu\text{m}$) but much smaller than that of the YAG laser ($\sim 80 \mu\text{m}$), so that only well-aligned molecules were pumped by the 267 nm pulse whilst avoiding strong-field ionization. The delay in time between the Ti:Sa pump and FEL probe pulses was varied using a delay stage.

The resulting charged particles were extracted from the interaction and towards their respective detectors using the voltages detailed in Chapter 7 for the 11.6 nm data. The ion detector had the same voltage differences applied to it as those described in

Section 7.2 of the previous chapter. Briefly, a voltage difference of around 1750 V was applied across the MCPs, while a voltage difference of around 2400 V was used between the back face of the back MCP and the phosphor screen. The flashes of light emitted from the back of the P47 phosphor screen were recorded with either a conventional CCD camera or PImMS1 camera. The measurements presented in this chapter were recorded at a repetition rate of 10 Hz.

8.2.2 Data Analysis

A detailed description of the data analysis procedure is given in the rest of this section. The procedure is based on Reference [84] and corrects for intensity artefacts and improves the temporal resolution, both of which are affected by fluctuations in the FEL pulse energy, arrival-time and its synchronization to the TiSa optical pulse. The FEL's pulse energy, bunch arrival-time monitor (BAM) and streak camera values are shown in Figure 8.1 (a) - (c), with the latter averaged over 20 FEL shots. Shot-to-shot fluctuations in the FEL's pulse energy and arrival-time over the first 100 FEL shots are clearly visible in panels (d) and (e). In the latter, the arrival-time jitter between the FEL pulse and the optical laser pulse is recorded for each FEL shot over a 4 ps range with a temporal resolution of ~ 10 fs (RMS) [172]. The streak camera monitors the arrival-time jitter over a longer timescale than the BAM, with a working range of 4 ps–80 ps and a temporal resolution of ~ 200 fs (RMS) [168]. In Figure 8.1(f), data recorded by the camera every two seconds (*i.e.* every 20 FEL shots) is shown for the first 100 FEL shots. Although the streak camera was not used in the shot-to-shot timing correction, it does act as a useful diagnostic tool to monitor timing drifts caused by long-term fluctuations in the FLASH synchronization system.

Here, the data analysis steps are detailed using an exemplary UV-laser pump and XUV-FEL probe measurement carried out on 1D-aligned 2,6-difluoriodobenzene (DFIB) molecules. In these measurements, approximately 1000 FEL shots of ion data were recorded at a series of pump-probe delays by moving the delaystage in steps of 100 fs. As previously mentioned, the UV pulse initiates the dissociation of the carbon-iodine bond in the molecule to generate two fragments, and either one or both of the

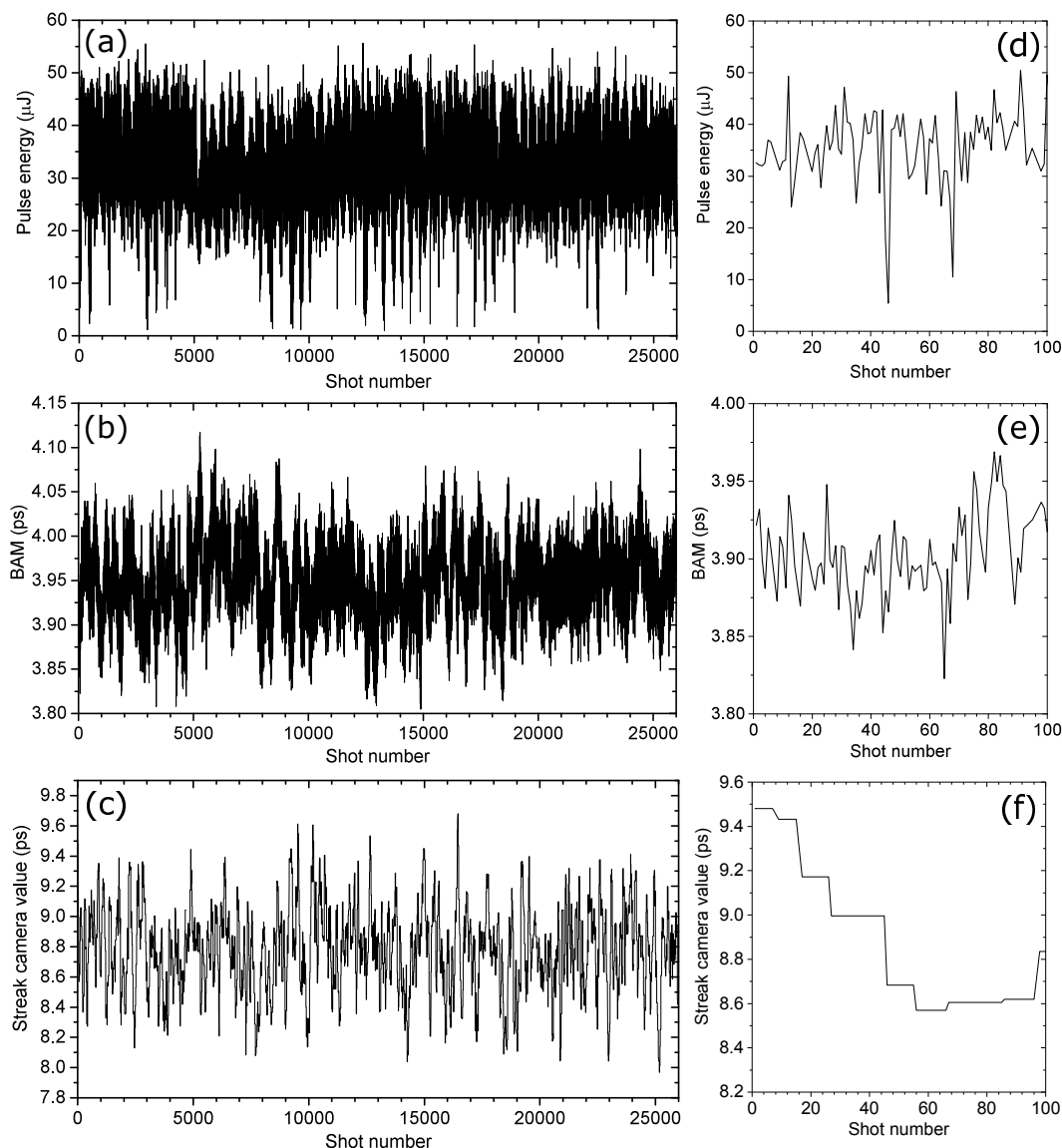


Figure 8.1: The shot-to-shot variations in (a) FEL pulse energy (b) beam arrival monitor (BAM) and (c) the streak camera value are shown as a function of FEL shot number for a complete scan corresponding to the UV-laser pump and XUV-FEL probe of 1D-aligned 2,6-difluoriodobenzene. Both (a) and (b) were recorded at a repetition rate of 10 Hz whilst (c) was recorded at 0.5 Hz. Panels (d) - (f) show zoom-ins of the first 100 FEL shots for the corresponding data shown in panels (a) - (c).

resulting fragments are then ionized by the XUV pulse. A typical pump-probe signal involves the appearance of a low kinetic energy release (KER) channel in multiply charged iodine fragments which are accompanied by a neutral co-fragment. As there is no Coulomb repulsion between these two fragments, the iodine fragment is ejected with a kinetic energy purely due to the photodissociation process. Figure 8.2 shows the delay-dependent ion yield of I^{3+} ions generated with low kinetic energies and partnered with a neutral co-fragment. Panel (a) shows the sum of all ion counts at each

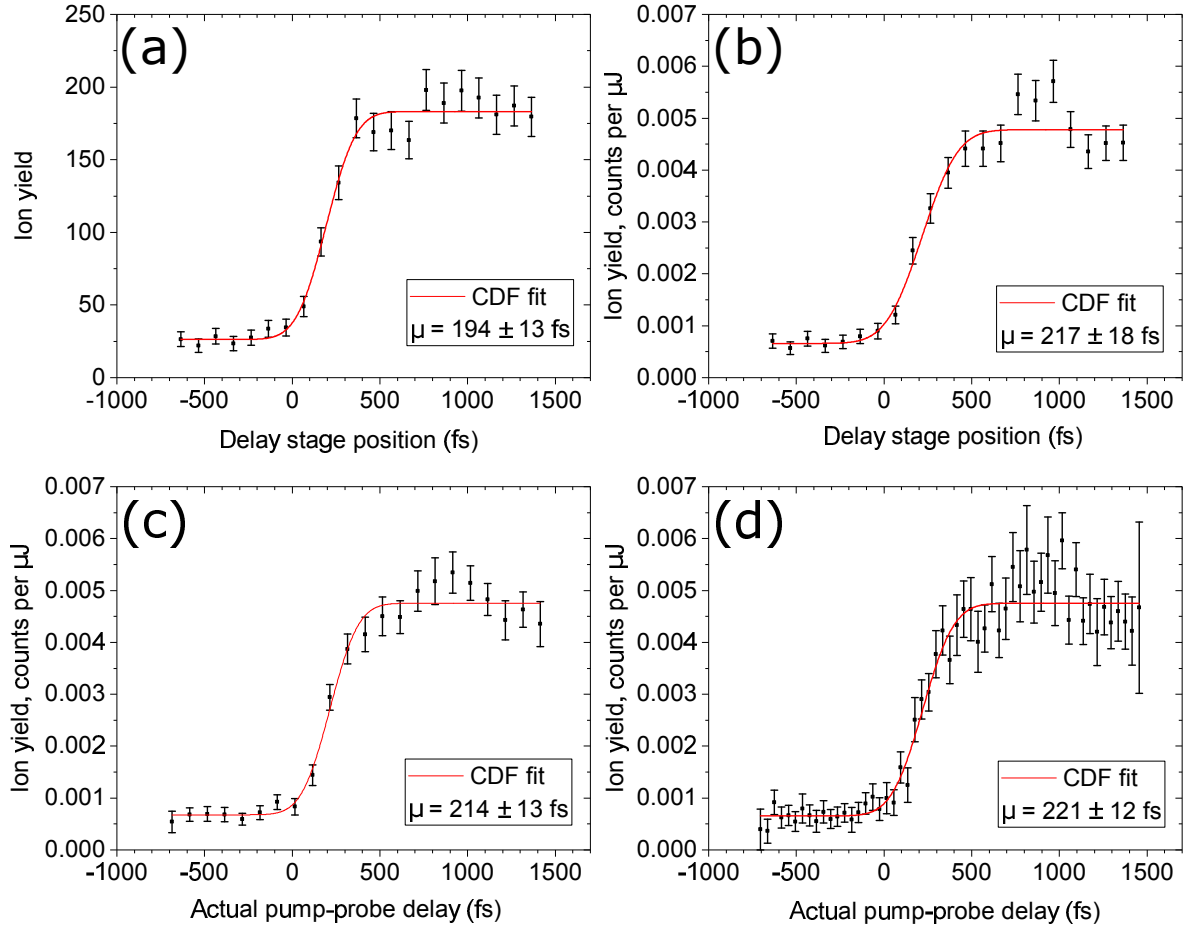


Figure 8.2: Delay-dependent yield of the low KER channel of I^{3+} ions generated after UV-laser photodissociation and XUV-FEL ionization of 1D-aligned 2,6-difluoriodobenzene molecules recorded with the PImMS1 camera. Here, positive (negative) delays correspond to the UV pulse reaching the molecule before (after) the XUV pulse. (a) Raw ion yield with no corrections applied to the data. (b) Same as (a) but normalised on the integrated FEL pulse energy at each delay step. (c) Same as (b) but with an additional arrival-time jitter correction applied to the data based on the shot-to-shot BAM data, and binned into 100 fs steps to give the ion yield as a function of the actual pump-probe delay. (d) Same as (c) but with the data re-binned into 40 fs steps. The red lines represent Gaussian cumulative distribution function (CDF) fits, with the centre position given by μ along with the fitting error.

delay without any corrections applied to the data. Positive (negative) delays correspond to the UV pulse interacting with the molecule before (after) the XUV pulse, and are referred to as UV early (late). At UV late delays, the channel of interest is not present since the molecule is still intact, while at UV early delays the dissociation of the molecule leads to the onset of the channel which appears as a step-function in the I^{3+} ion yield. This can be modelled by a Gaussian cumulative distribution function

$$f(x) = A + B \operatorname{erf} \left(\frac{x - \mu}{\sigma} \right), \quad (8.1)$$

where A and B are the baseline and amplitude, respectively, erf is the Gaussian error function, and μ and σ are the centre position and temporal width of the step function, respectively.

FEL Pulse Energy Normalisation

Although the raw ion yield looks relatively stable, the data is influenced by fluctuations in the FEL pulse energy and the arrival-time jitter that exists between the XUV and UV pulses, and must be corrected for to extract reliable timescales from FEL-related pump-probe data. First, the pump-probe data is corrected for fluctuations in the FEL's pulse energy. Figure 8.3(a) shows a linear dependence between the total ion yield and the FEL pulse energy on a shot-to-shot basis. By applying a global shift to the BunchID (*i.e.* the unique identifier for each FEL shot) in the data of +1 or -1, the correlation is reduced as shown in panels (b) and (c), respectively. To account for fluctuations in the FEL pulse energy, the sum of the ion counts was normalised by the integrated value of the pulse energy at each delay, shown in Figure 8.3(d), to produce an energy-normalised ion yield as in Figure 8.2(b). In this plot, the values at approximately 700-900 fs appear to be slightly higher than expected, and coincide with fluctuations in the arrival-time jitter between the FEL and laser pulses.

FEL Arrival-Time Jitter Correction

The frequency distribution of the bunch arrival-time monitor (BAM) data is shown as a histogram in Figure 8.4(a). The mean of the distribution, μ_B , was determined to be 3.95 ps after application of a Gaussian fit (blue solid line). The width of the Gaussian fit was 92 fs (FWHM) and represents the timing jitter of the electron bunches in the FEL with respect to the master oscillator. In Figure 8.4(b), the average BAM value at each delay clearly fluctuates above and below the mean of the distribution (red dashed line). In particular, the average BAM value is higher than expected at delays of 800-900 fs, which is around the same delay region as the artefacts present in the ion yield seen in Figure 8.2(b). A correction for the arrival-time jitter is applied on a shot-to-shot basis by first calculating the difference, $\Delta t_B(i)$, between the BAM value,

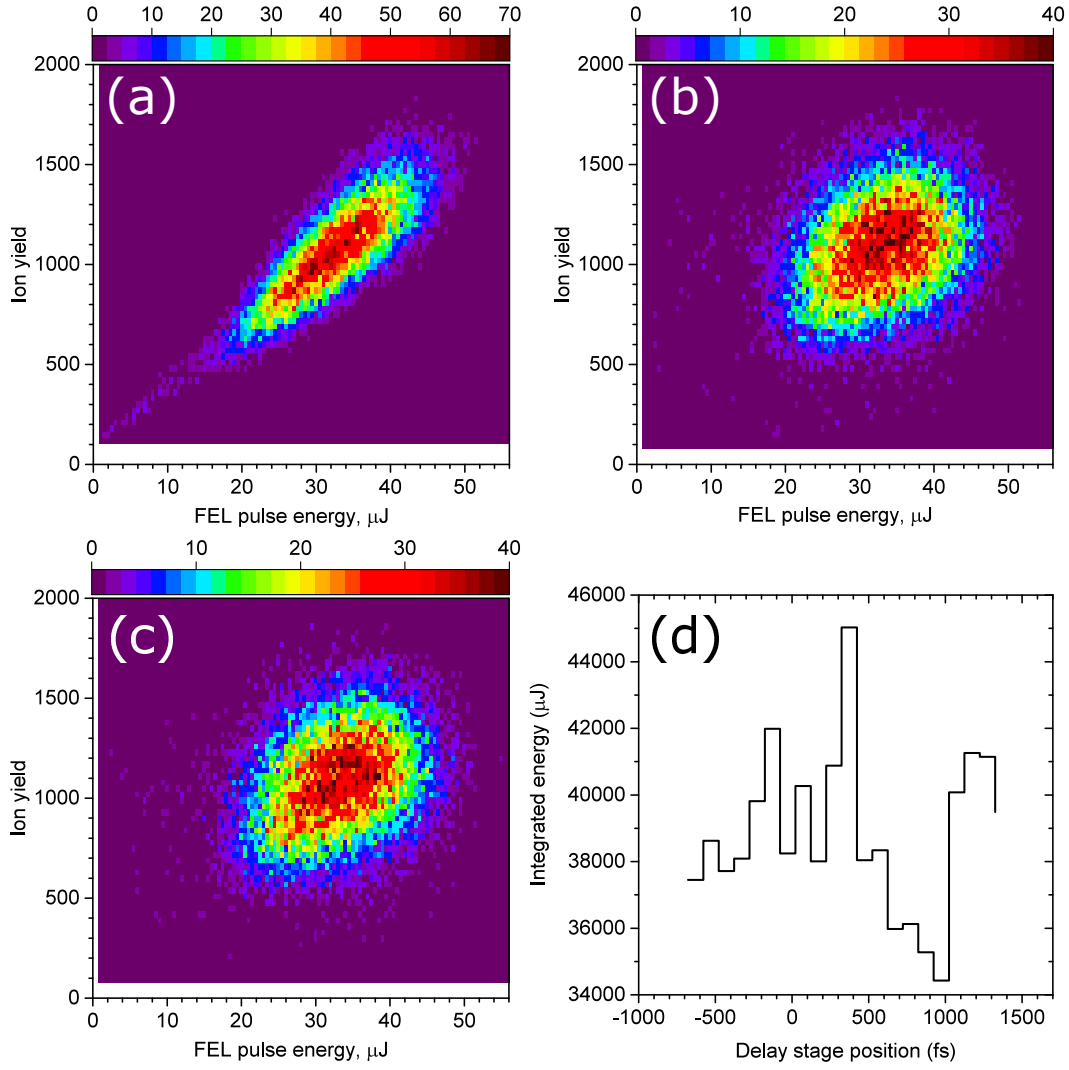


Figure 8.3: (a) Two-dimensional map showing the linear dependence of ion yield with the FEL pulse energy. Parts (b) and (c) are similar to part (a) but with a global shift of +1 and -1 applied to the BunchID (*i.e.* the unique identifier for each FEL shot), respectively, which yields less well correlated maps. (d) The integrated value of the FEL pulse energy is shown for each delay stage position.

$t_B(i)$, and the mean BAM value, μ_B , as described by

$$\Delta t_B(i) = t_B(i) - \mu_B \quad (8.2)$$

for a particular FEL shot, i , which is then added to the delay stage position, t_d , to yield the actual pump-probe delay, $t_r(i)$, as given by

$$t_r(i) = t_d + \Delta t_B(i). \quad (8.3)$$

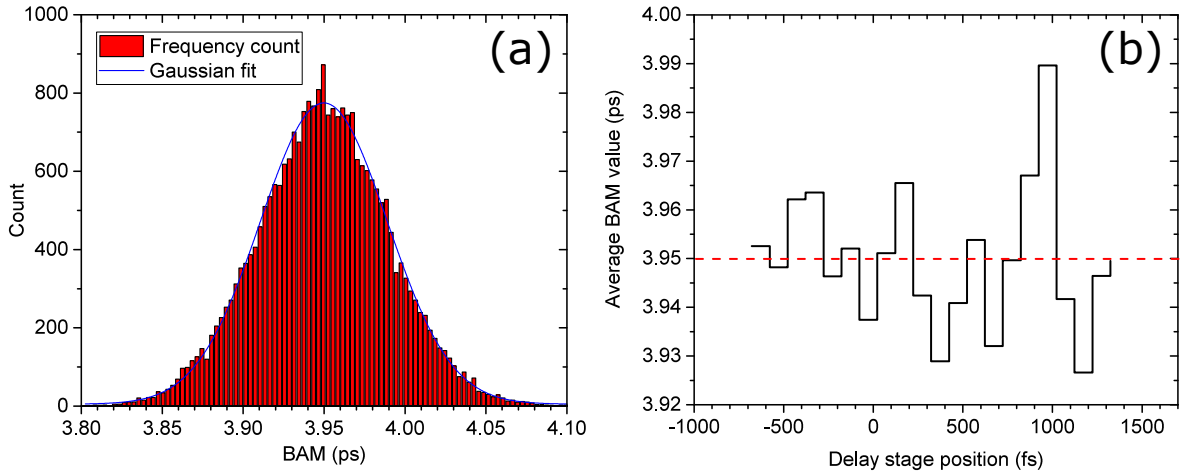


Figure 8.4: (a) Histogram distribution of the BAM data shown in Figure 8.1(b), with a Gaussian distribution fit applied (blue solid trace). (b) The average BAM value at each delay stage position, with the red dashed trace representing the mean of the Gaussian fit (3.95 ps) applied to the histogram distribution in (a).

The outcome of this correction is shown in Figure 8.5 with both the BAM-corrected (black solid line) and the nominally set (red solid line) delays plotted as a function of FEL shot number. Panel (b) shows a close-up of the overall scan for five nominally set delays, with the actual pump-probe delay appearing on average at more positive delays than in the nominally set delay.

The BAM-corrected data were then grouped into 100 fs bins to generate an ion yield with sufficient statistics shown in Figure 8.2(c). Following the jitter-correction, the fluctuations at a delay of around 800 fs are suppressed, and the mid-point of the step-function, given by the mean (μ) of the Gaussian fit (red solid line), is 214 ± 13 fs which is approximately 20 fs later than in the raw distribution. Since the BAM value is recorded with a resolution of ~ 10 fs and the jitter-correction was applied on the shot-to-shot data, no restriction exists on the bin size that can be used to group the BAM-corrected data. Figure 8.2(d) shows the resulting ion yield distribution binned into 40 fs steps that gives a mean value of 221 ± 12 fs from the Gaussian fit, which is 27 fs later than in the raw distribution. The choice of bin size is a compromise between good statistics and the smallest bin size that can be used.

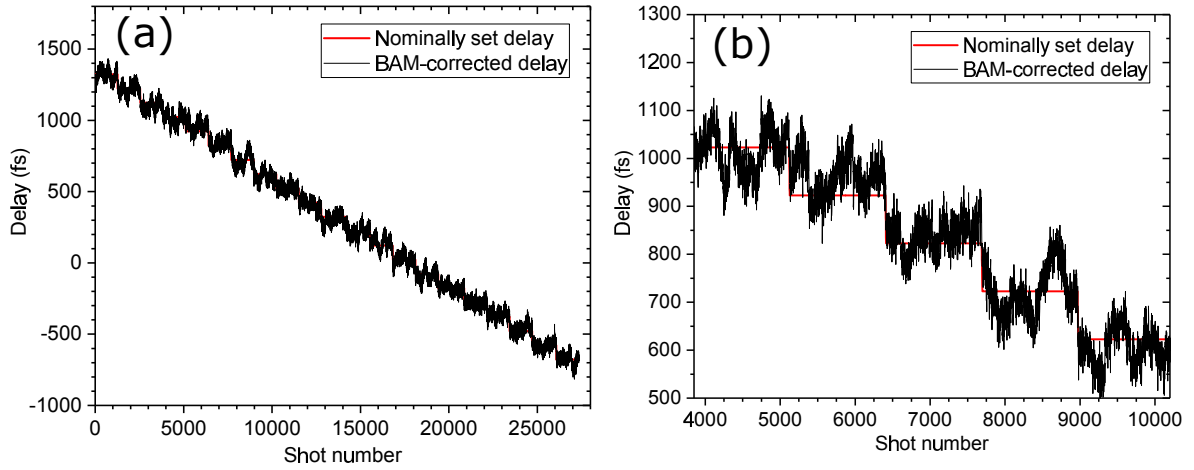


Figure 8.5: The BAM-corrected (black solid line) and nominally set (red solid line) delays as a function of FEL shot number are shown for the (a) whole scan and for (b) five nominally set delays recorded at the start of the scan. The actual pump-probe delays are given by the black line and have much higher precision than in the nominally set delay.

Streak Camera Value

In this section, the streak camera is used to filter data with any sudden temporary shift in the actual pump-probe delay that is on the order of picoseconds. An example dataset, recorded with a CCD camera and analysed by Evgeny Savelyev, is presented. The data set contains significant artefacts and oscillations in its raw delay-dependent ion yield as shown in Figure 8.6(a). Normalising the raw data against the integrated FEL pulse energy does lead to a slight dampening of artefacts although these are still present as shown in panel (b). This is unsurprising given that there was no significant fluctuation in the integrated FEL pulse energy as a function of delay stage position shown in Figure 8.7(a). However, there are significant fluctuations in the BAM value as shown in Figure 8.7(b).

The delay before (red solid line) and after (black solid line) the jitter-correction is shown in Figure 8.7(c). The resulting BAM-corrected data, shown in Figure 8.6(c), is grouped in 30 fs bins, with all artefacts corrected for, apart from one unexpected feature at a delay of approximately -200 fs. This feature is due to a large rise in the raw streak camera values (black solid trace) that span tens of picoseconds around shot number 6350 (which corresponds to the delay of -200 to -400 fs), as shown in Figure 8.8. This rise coincided with a large rise in the jitter between the pump-probe laser and

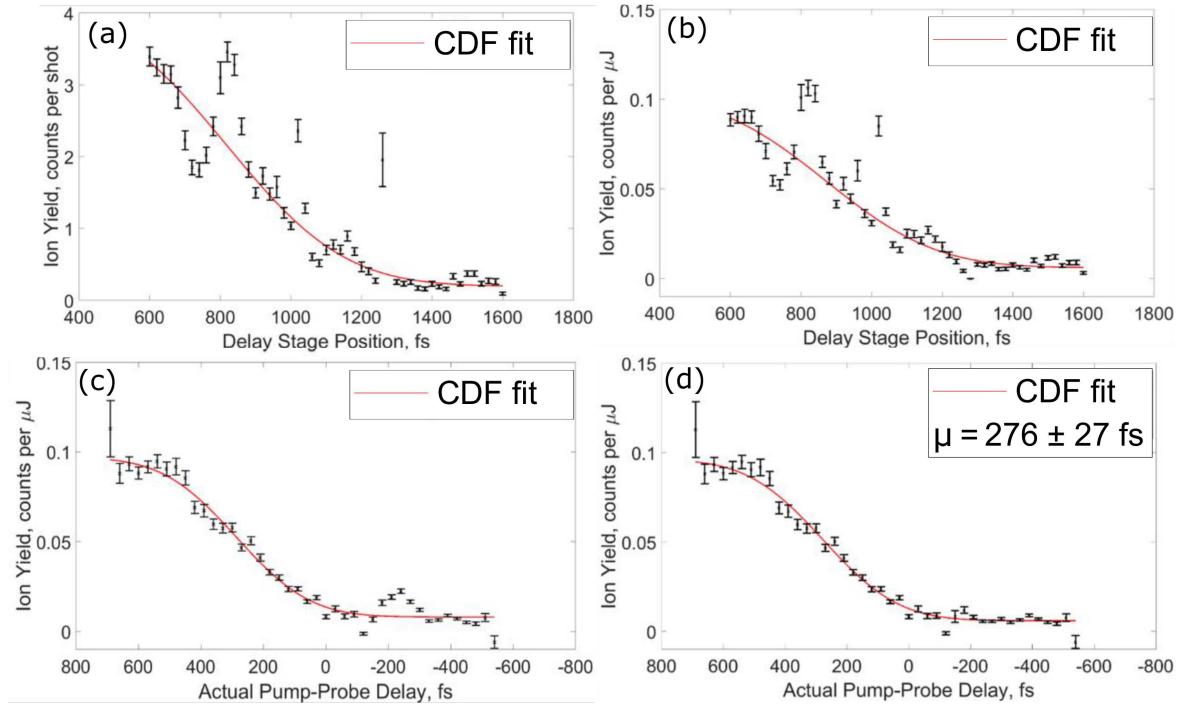


Figure 8.6: Delay-dependent yield of the low KER channel from I^{3+} ions generated after UV-laser photodissociation and XUV-FEL ionization of 3D-aligned 2,6-difluoriodobenzene molecules recorded with a conventional CCD camera. Here, positive (negative) delays correspond to the UV pulse reaching the molecule before (after) the XUV pulse. (a) Raw ion yield only normalised by the number of laser shots at each delay. (b) Same as (a) but normalised on the integrated FEL pulse energy at each delay step. (c) Same as (b) but with an additional arrival-time jitter correction applied to the data based on the shot-to-shot BAM data, and binned into 30 fs steps to give the ion yield as a function of the actual pump-probe delay. (d) Same as (c) but with data removed due to the sudden jump in the streak camera value. The red lines represent Gaussian cumulative distribution function (CDF) fits to each ion yield distribution, with the mean of the fit given by μ . This figure was adapted from Reference [84].

the master laser oscillator (blue dashed trace) using the optical cross-correlator. As a consequence of the temporary failure in the laser synchronization system, the actual pump-probe delay was temporarily shifted from UV late delays to UV early delays, recording a relatively large ion signal at the delay of -300 fs. The subset of data that lead to this jump in streak camera values was removed from the data set to generate the final delay-dependent yield shown in Figure 8.6(d), with the artefact seen in (c) accounted for in (d).

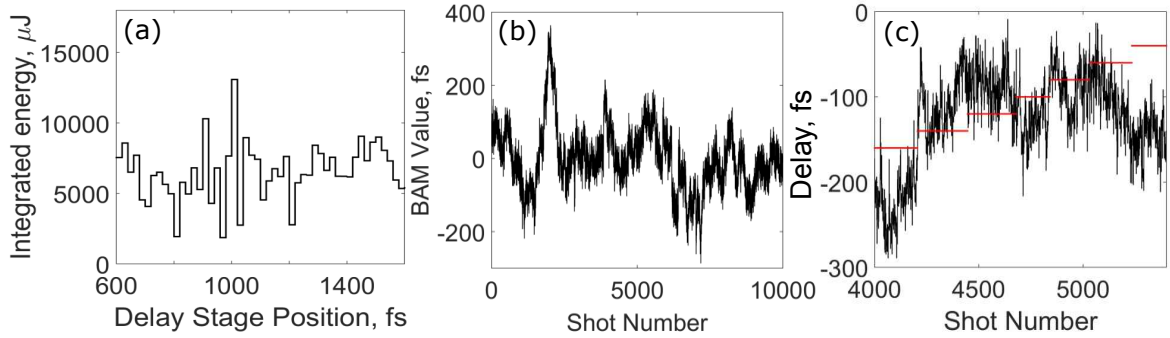


Figure 8.7: (a) The integrated value of FEL pulse energy as a function of delay stage position. (b) The BAM value as a function of shot number. (c) The BAM-corrected (black solid line) and nominally set (red solid line) delays as a function of FEL shot number shown for a portion of the full scan corresponding to seven nominally delays recorded in the middle of the scan. This figure was adapted from Reference [84].

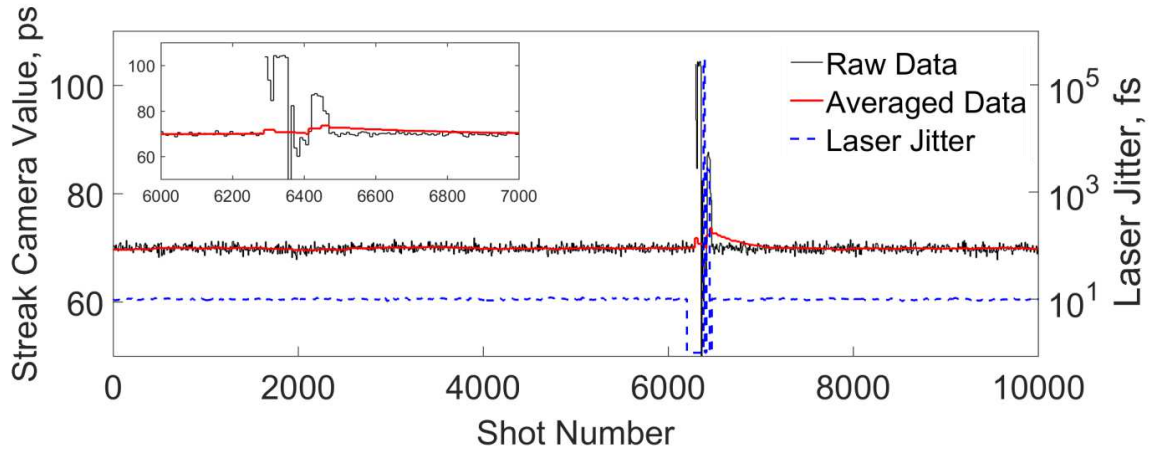


Figure 8.8: The raw (black solid line) and averaged (red solid line) streak camera values shown for the entire scan. The jitter between the pump-probe laser and the master laser oscillator was recorded simultaneously using the optical cross-correlator and is shown as a dashed blue line. The inset shows a jump in the laser jitter around shot number 6350 corresponding to a temporary failure of the laser synchronization system. This figure was adapted from Reference [84].

8.3 Photodissociation of CH₃I and Subsequent Inner-Shell Ionization

Results from a proof-of-principle experiment are presented in this section that couples a fast imaging sensor, the PImMS1 camera, with time-dependent UV-pump and XUV-probe experiments on laser-aligned methyl iodide. Photodissociation and charge transfer dynamics were imaged on the femtosecond timescale at the Free-Electron Laser in Hamburg (FLASH) facility in DESY. Results from this work are compared to previous UV-Xray and NIR-Xray measurements on unaligned CH₃I [77, 81].

As discussed previously in Chapter 7, the XUV (107 eV) pulse leads to the inner-shell ionization of CH₃I occurs at the iodine site of the molecule. The initial charge is strongly localized on the iodine site, and then spreads to the rest of the molecule within the pulse duration of the FEL to induce a Coulomb explosion of the molecule [77, 81]. The initial velocities of the fragment ions are projected onto a position- and time-sensitive detector using VMI, with the position and time-of-arrival of all ions recorded simultaneously by the PImMS1time-stamping camera. In this chapter, the multi-mass capability of the PImMS1camera is extended to dynamic studies through time-resolved pump-probe measurements, as detailed in the following sections.

8.3.1 Pump-Probe Effects

In the rest of this chapter, results from time-resolved pump-probe measurements are presented. A femtosecond UV “pump” pulse (267 ± 2.5 nm) initiates the photodissociation of the carbon-iodine bond; the resulting fragments are ionized with an intense, femtosecond XUV “probe” pulse (11.6 ± 0.56 nm) from the FLASH FEL. By recording data at various fixed delays between the two pulses, a series of snapshots of the molecule can be recorded to generate a “molecular movie” of the photo-induced reaction. Figure 8.9 shows the ToF spectrum recorded by the PImMS1camera at UV early delays (*i.e.* the molecule interacts with the UV pulse before the XUV pulse) and UV late delays (*i.e.* the molecule interacts with the UV pulse after the XUV pulse). Ion images corresponding to the shaded ToF profiles are shown above the ToF spectrum.

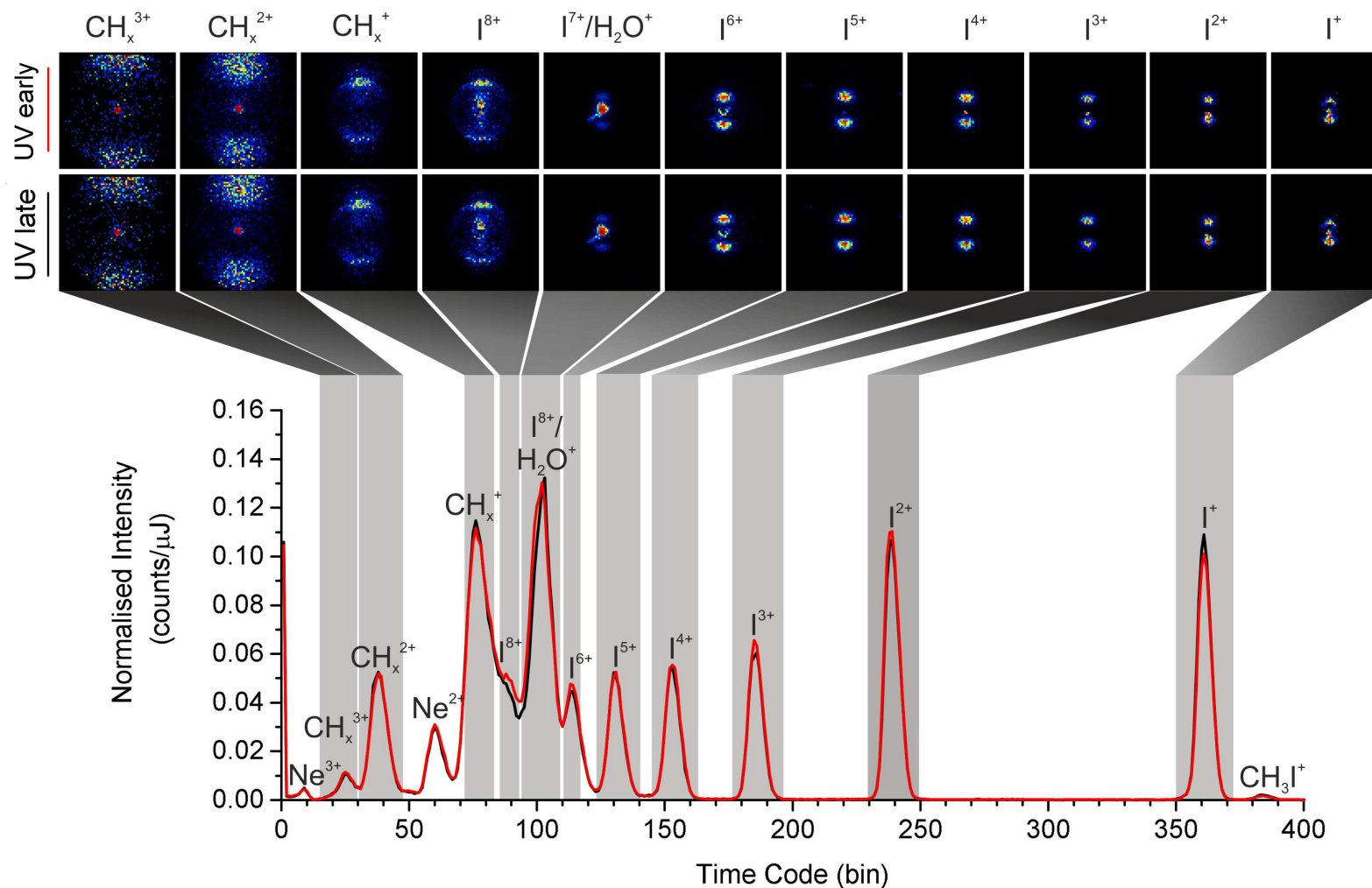
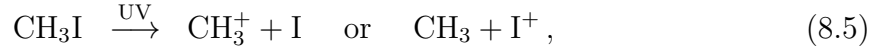


Figure 8.9: Time-of-flight spectrum showing the ions formed after the absorption of UV photon(s) either before (UV early, red solid trace) or after (UV late, black solid trace) the absorption of XUV photons by 1D-aligned CH_3I molecules. Assignments for each peak are shown, with the ion images for the shaded grey ToF peaks shown above the ToF spectrum for both UV early (top) and UV late (bottom) measurements. All data were recorded with the PImMS1 camera.

In the case where the UV pulse is absorbed by the molecule first, two neutral fragments are generated, according to



and it could also, theoretically, generate one charged fragment,

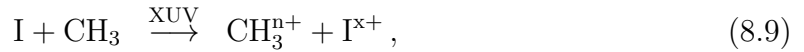
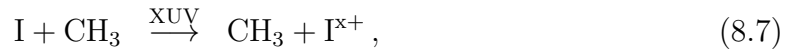


or two charged fragments,



depending on the intensity of the UV pulse. At the intensity of the UV pulse used in these measurements, it is highly unlikely that both fragments were charged. In the neutral dissociation case, the singly charged case can, theoretically, be distinguished from the purely neutral case by comparison of their asymptotic energies. Although the asymptotic energy for the singly neutral case (*i.e.* $\text{CH}_3^+ + \text{I}$ or $\text{CH}_3 + \text{I}^{x+}$) is not known for CH_3I , the asymptotic energy for the neutral case has been previously reported by Eppink and Parker in the one-photon resonant neutral dissociation of CH_3I at 267 nm [15, 16].

The XUV pulse can ionize either the iodine, methyl or both fragments, as given by



where x and n are the charges on the iodine and CH_3 fragments, respectively. If either

one or both of the fragments are neutral after the interaction of molecule with the UV and XUV pulses, then both fragments are ejected with low kinetic energies that are characteristic of only the photodissociation process due to the lack of Coulomb repulsion between the two fragments. This is denoted the $(0, x)$ channel, corresponding to a neutral co-fragment and either a neutral or charged iodine.

At UV early delays, iodine fragments with low kinetic energy appear as a central spot in the corresponding ion image. This is clearly observed in Figure 8.10(a) for the I^{3+} ion when inspecting the UV early (left) and UV late (middle) ion images. The difference ion image (right) shows the appearance of a central spot at early delays, accompanied by a slight decrease in the yield of the high KER channel at larger radii. These changes in both KER channels are visible in the corresponding radial distributions shown in panel (b) for UV early (red line) and UV late (black line) delays.

It should be noted that in the upper half of the UV early ion image, the low KER channel is not present due to the saturation of the corresponding PImMS1 pixels by the arrival of lighter fragments before the I^{3+} ion. Therefore, in the rest of this section, only the bottom half of the detector image for iodine fragments is analysed. By recording a small amount of data (~ 1000 shots) at a series of pump-probe delays (in steps of ~ 100 fs); the radial (and hence kinetic energy) distribution can be extracted from the corresponding ion images to generate a time-dependent “map” of the radii at which the features appear.

Figure 8.10(c) shows the delay-dependent radial distribution for I^{3+} ions, recorded with the PImMS1 camera, with two distinct KER channels present: the $(0, x)$ and the ‘intact molecule’ channels. Panel (b) shows that the $(0, x)$ channel is absent at negative (UV late) delays (black squares) but present at positive (UV early) delays (red circles). The onset of the $(0, x)$ channel appears as a step-function as shown by the corresponding integrated ion yield (black line) as a function of time delay in panel (d). The intact KER channel is equivalent to the “probe-only” channel, where either the molecule remains intact after the absorption of UV photons or does not interact with the UV pulse. Thus, the ‘intact molecule’ is ionized by the XUV pulse, generating a highly unstable multiply charged molecular ion that Coulomb explodes.

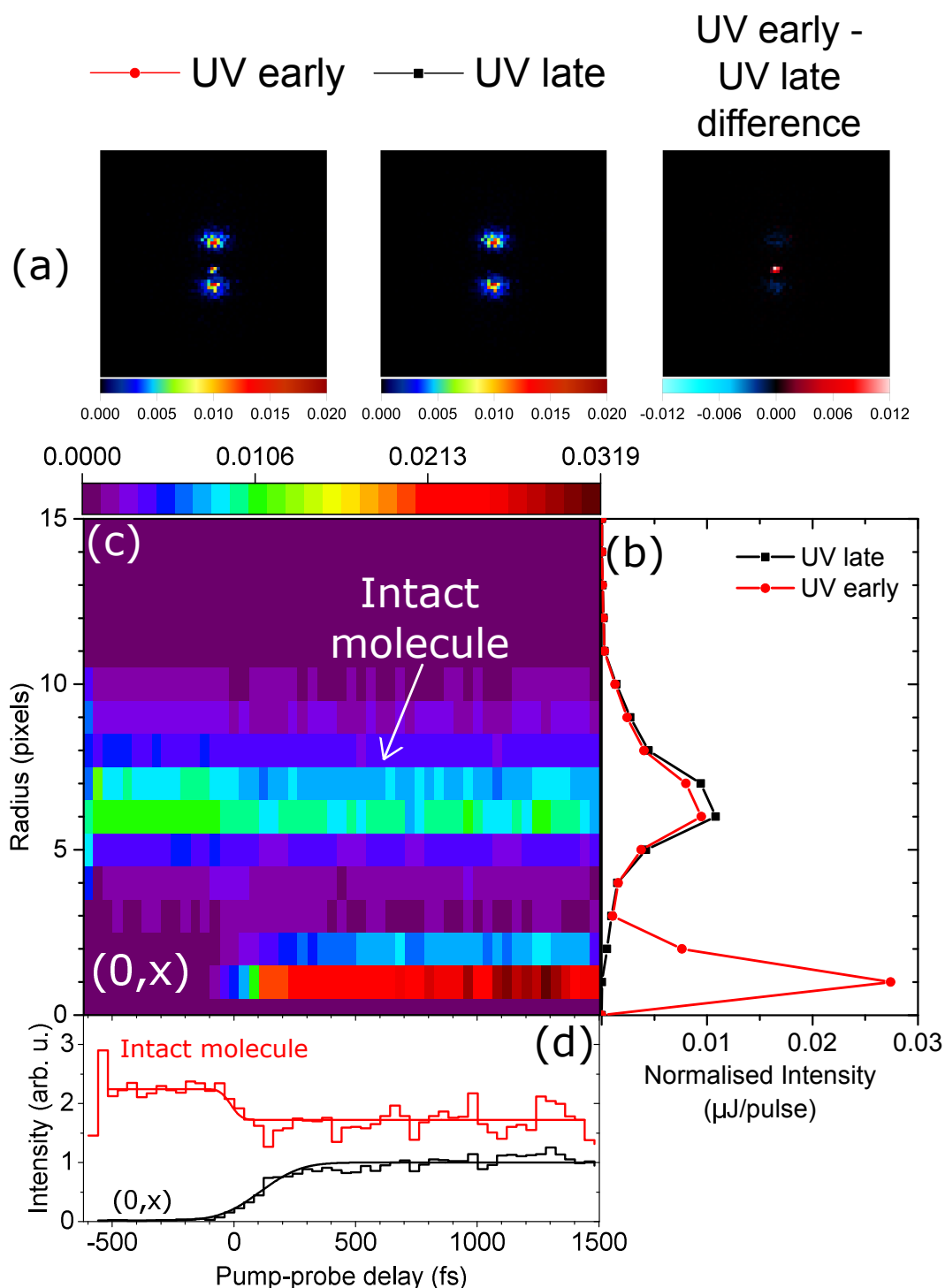


Figure 8.10: (a) I^{3+} ion images, recorded with the PImMS1 camera, corresponding to the UV early (left), UV early (middle), and “UV early - UV late” difference (right) are shown. (b) Integrated radial distributions at five UV early (red circle line) and five UV late (black square line) delays corresponding to the ion images in panel (a). (c) Map of the delay-dependent radial distribution of I^{3+} ions from the UV-laser photodissociation and XUV-FEL ionization of 1D-aligned CH_3I molecules. Panel (d) shows the I^{3+} ion yield of the (0, x) and the ‘intact molecule’ KER channels. For both channels, the signal is fitted with a Gaussian cumulative distribution function. The data in each delay bin were normalised to the sum of the FEL pulse energy, and a jitter-correction was also applied as outlined in Ref. [84].

The resulting charged fragments are ejected with relatively large kinetic energies as a result of the Coulomb force between them. A small decrease in the corresponding integrated ion yield is seen with increasing pump-probe delay, due to a reduction in the target molecules as some of the molecules are dissociated by the UV pulse, known as the target depletion effect.

The corresponding high-resolution delay-dependent map recorded with a CCD camera is shown in Figure 8.11(a) and (b), with the latter a close-up of the former in the region of 0-1 eV. The resulting radial distributions were converted to a kinetic energy scale using a simulation of the VMI spectrometer performed in SIMION [173]. In panel (b), the low KER channel can be resolved to reveal two sub-components which correspond to the spin-orbit splitting of iodine, where a neutral cofragment is generated with an iodine atom either in its ground or electronically excited state as shown by the potential energy surface sketch in panel (d).

In Figure 8.11(b), the calculated kinetic energies for I (white dotted trace) and I* (white dashed trace) following the UV-induced dissociation of CH₃I are shown. The kinetic energy was calculated using the following procedure. Knowing the dissociation energy, D_0 , (2.41 eV for CH₃I [15]), and the energy of one pump photon, $E_{h\nu}$, (267 nm, 4.65 eV) used to dissociate the molecule, the total available energy remaining in the molecule, E_{avl} , is given by

$$E_{avl} = E_{h\nu} - D_0. \quad (8.10)$$

A second kinetic energy channel may be observed due to the spin-orbit splitting of a fragment in the molecule, such as the iodine atom in CH₃I, as described by

$$E_{avl*} = E_{avl} - E_{SO}, \quad (8.11)$$

where E_{SO} is the spin-orbit splitting (0.943 eV for iodine in CH₃I at 267 nm [15]). Since energy is conserved, the total available energy is also equal to the sum of the product

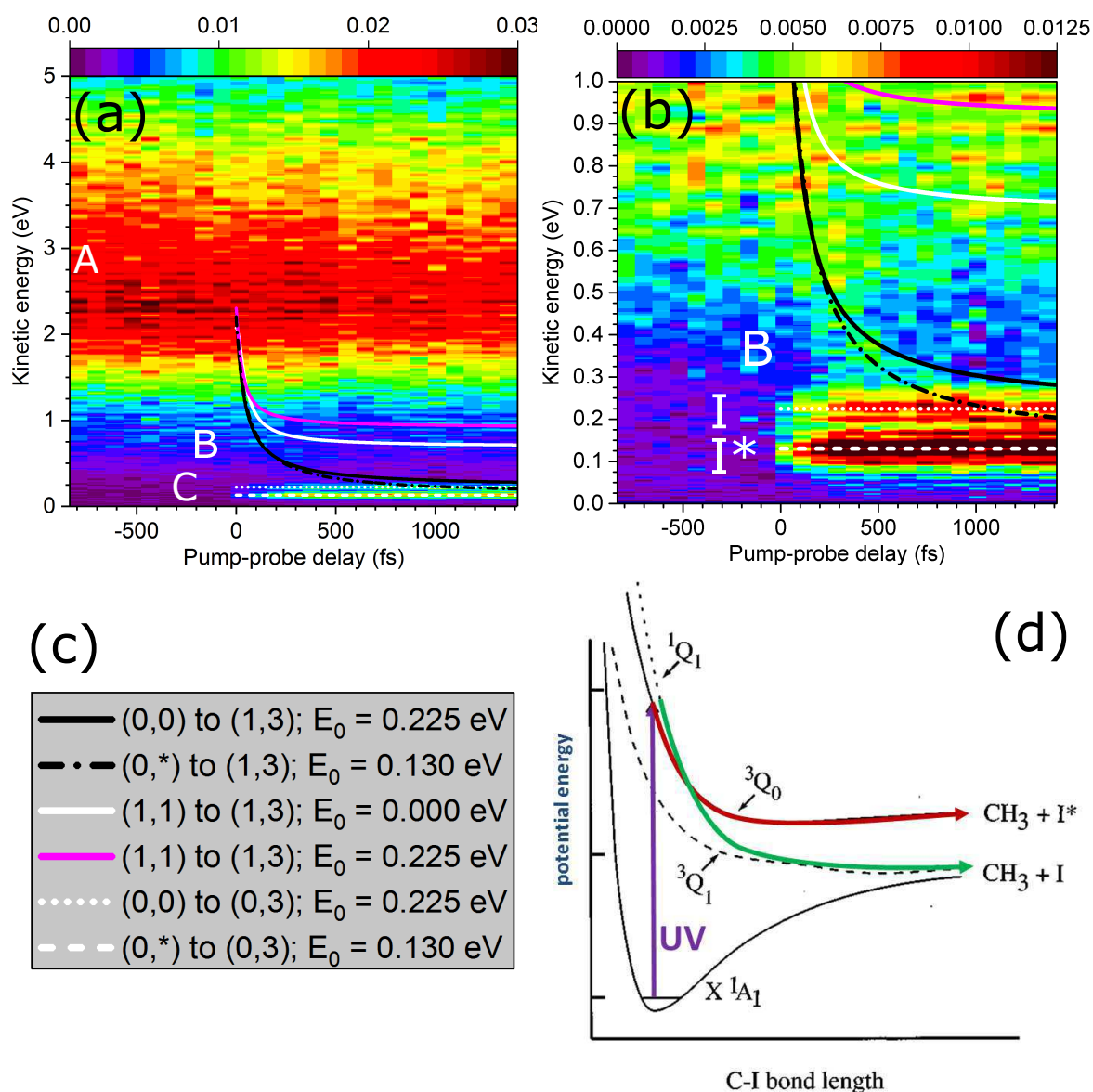


Figure 8.11: (a) Delay-dependent radial distribution map of I^{3+} ions following the UV-laser photodissociation and XUV-FEL ionization of 1D-aligned CH_3I molecules recorded with a high-resolution CCD camera. (b) A zoom-in of panel (a) between the kinetic energy range of 0-1 eV. The spin-orbit splitting of the UV dissociation channel is resolved, and is shown in labels “I” and “I*”. The “intact” channel and the Coulomb channel are marked as features A and B, respectively. Simulated Coulomb curves are shown for the neutral dissociation of CH_3I that generate either I (black solid trace) or I* (black dash-dot trace), while the charged dissociation case is also shown for I^+ generated with an initial kinetic energy of either 0.00 eV (white solid trace) or 0.225 eV (magenta solid trace). The calculated kinetic energy of the (0, x) channel for I (white dot trace) and I* (white dash trace) are also shown. Experimental data shown in this figure was pulse energy and BAM corrected by Evgeny Savelyev. Panel (c) shows the legend corresponding to panels (a) and (b). Panel (d) shows the potential energy surfaces involved in the UV-induced dissociation of CH_3I , and was adapted from Reference [16].

translational energy, E'_{trans} , and the CH_3 internal excitation, E'_{int} , as described by

$$E_{\text{avl}} = E'_{\text{trans}} + E'_{\text{int}}. \quad (8.12)$$

The proportion of total available energy transferred into translational energy is given by

$$f_{\text{trans}} = \frac{E'_{\text{trans}}}{E_{\text{avl}}}. \quad (8.13)$$

Accounting for conservation of momentum, the calculated maximum kinetic energy release for I and I* fragments is 0.24 eV and 0.14 eV, respectively, following the one-photon photodissociation of CH_3I at 266 nm. Previous work by Eppink and Parker at 267 nm reported kinetic energies of 0.24 eV and 0.14 eV for I and I*, respectively [15]. Their kinetic energies correspond to f_{trans} values of 1.0 for both I and I*. Work by Zhu *et al.* [321] at 248 nm reported f_{trans} values of 0.83 and 0.87 for I and I* in CH_3I , respectively. In the work presented in this chapter, the extracted mean KER of the I (white dotted trace) and I* (white dashed trace) channels (shown in Figure 8.11(b)) were 0.225 eV and 0.130 eV, respectively, and agree with those reported by Eppink and Parker at 267 nm [15]. The kinetic energies of I and I* from the work presented in this chapter correspond to f_{trans} values of 0.95 for both I and I*, which is approximately 5% smaller than in the work by Eppink and Parker at 267 nm [15].

The I* channel (white dotted trace) is stronger than the I (white dashed trace) channel as shown in Figure 8.11(b), and this is quantified by the I* quantum yield described by

$$\Phi^* = \frac{I(\text{I}^*)}{I(\text{I}) + I(\text{I}^*)}, \quad (8.14)$$

where $I(\text{I}^*)$ and $I(\text{I})$ are the integrated signals corresponding to the I* and I channels, respectively. A Φ^* value of 0.61 was extracted from the experimental data shown in Figure 8.11(b). Previous Φ^* values of 0.68-0.89 have been reported by several authors [16, 322–325].

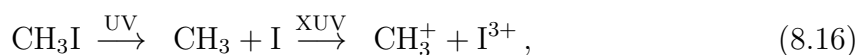
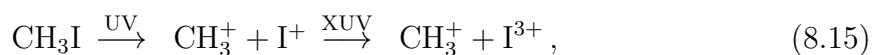
A second time-dependent KER channel, marked as feature B, is observed in Figure

8.11(b). This feature corresponds to the ejection of the I^{3+} ion with a singly charged co-fragment (CH_3^+) following the absorption of both UV and XUV photons, as shown in Equation (8.9). At a delay of 0 fs, both the UV and XUV pulses arrive at the same point in time, t_0 , and this serves as the start time of the photo-induced dissociation reaction.

At positive time delays close to t_0 , the distance between the two resulting fragments will be similar to that in the intact molecule since the fragments did not have enough time to fly away from each other before ionization by the XUV pulse. Thus, the strong Coulombic repulsion between the separating fragments leads to charged products with large kinetic energies. In these time-resolved experiments, the pump-probe delay, τ , corresponds to the distance between the two fragments. The larger (smaller) τ the further (closer) the fragments are to each another leading to a weaker (stronger) Coulomb explosion and the ejection of fragments with lower (higher) kinetic energies. Thus, this is referred to as the Coulomb channel.

The Coulomb channel can be simulated by solving Newton's equations of motion, which allows an investigation into the charge states of the fragments to be determined after the interaction of the molecule with the UV pulse (referred to as step 1) and the XUV pulse (referred to as step 2). Simulation of the Coulomb channel can also be used to determine t_0 in measurements where a cross-correlation signal is absent, which is the case in the measurements presented in this chapter.

Four simulated Coulomb curves are shown in Figure 8.11(a) and (b), and correspond to the neutral and charged dissociation of CH_3I induced by the UV pulse followed by ionization of the fragments by the XUV pulse. The two UV-XUV reaction schemes simulated for the neutral and charged UV dissociation cases is given by Equations (8.15) and (8.16), respectively.



In the charged dissociation case, given by Equation (8.15), two simulated curves are shown in Figure 8.11(a) where the charged fragments are created with zero initial velocity (*i.e.* $E_0 = 0$ eV, white solid trace) or with an initial velocity corresponding to the asymptotic energy of the $\text{CH}_3 + \text{I}$ neutral channel (*i.e.* $E_0 = 0.225$ eV, magenta solid trace). The XUV pulse further ionizes the singly charged iodine to generate CH_3^+ and I^{3+} ions.

In the neutral dissociation case, given by Equation (8.16), the UV pulse generates two neutral fragments, with each curve shown in Figure 8.11(b) corresponding to the I ($E_0 = 0.225$ eV, black solid trace) and I^* ($E_0 = 0.130$ eV, black dash-dot trace) channels. Although it may be theoretically possible to generate one charged and one neutral fragment (*i.e.* $\text{CH}_3^{n+} + \text{I}$ or $\text{CH}_3 + \text{I}^{x+}$) with the UV pulse, the asymptotic energy of the $(n,0)$ or $(0,x)$ channels is not known, and so for simplicity sake, the simulation of the $(0,0)$ neutral dissociation case is only considered. In this neutral dissociation case, the neutral fragments are ionized by the XUV pulse to generate CH_3^+ and I^{3+} ions.

The simulated Coulomb curves for the neutral dissociation case clearly match the experimental feature B much better than the charged dissociation cases. In particular, the simulated curve corresponding to the $\text{CH}_3 + \text{I}^*$ channel provides an excellent match with the experimental Coulomb channel labelled as feature B. In contrast, both simulated curves for the charged case completely miss the experimental Coulomb channel, as observed in the top of Figure 8.11(b), since the resulting asymptotic energies are much too high. Thus, the Coulomb channel labelled as feature B in Figure 8.11(b) is assigned as the neutral dissociation of CH_3I through a one-photon process induced by the UV pulse, and the neutral fragments are then subsequently ionized by the XUV pulse to generate I^{3+} and CH_3^+ ions. Details of the procedure used to simulate these neutral and charged Coulomb curves is given in the following section.

8.3.2 Dissociation of CH_3I

The kinetic energies of two particles were calculated at various pump-probe delays, τ , by numerically solving Newton's equations of motion [83]. In the case where both

particles are charged, they experience repulsion between each other due to the presence of a Coulombic force, F_t , given by $F_t = ma_t$, where m is the mass of the particle and a_t is the acceleration of the particle at time t . Knowledge of the latter can be used to calculate the velocity of the particle, v_t , at time t , as described by

$$v_t = v_0 + a_t t, \quad (8.17)$$

where v_0 is the particle's initial velocity. The position of the particle, x_t , at time t is calculated using

$$x_t = x_0 + v_0 t + \frac{1}{2} a_t t^2, \quad (8.18)$$

where x_0 is the initial position of the particle. The equations of motion were solved by numerically integrating them using the Runge-Kutta fourth order method, with the choice of initial conditions playing a crucial role. As discussed previously, this experiment can be described by a two-step process: dissociation by the UV pulse, and ionization by the XUV pulse.

In the first process induced by the UV pulse, the initial positions of both particles are set to the equilibrium bond distance, r_{eq} , at $t = 0$ fs, their initial velocities are calculated using Equations (8.10)-(8.13) whilst taking into account conservation of momentum, and initial charges of q_1^i and q_2^i are used on both particles. The equations of motion are numerically solved between the time range of $(0, \tau)$ using the above mentioned initial conditions, referred to as Step 1 in Figure 8.12, through

$$\begin{aligned} \int_{t=0}^{t=\tau} \frac{dv}{dt} dt &= a \\ \int_{t=0}^{t=\tau} \frac{dx}{dt} dt &= v, \end{aligned} \quad (8.19)$$

where the velocity of the second particle is negative so that the two fragments fly in the opposite direction to conserve momentum in the system.

An increase in the distance between two charged fragments leads to a decrease in their potential energy, as shown by the green solid trace in Figure 8.12 corresponding

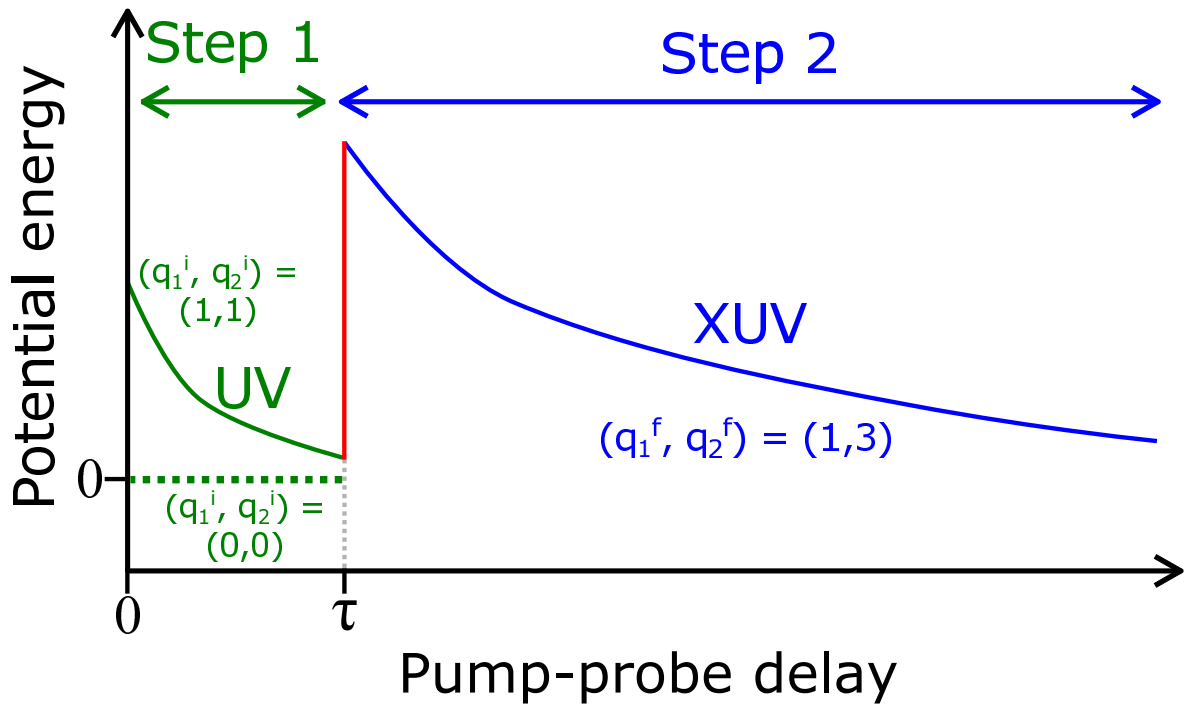


Figure 8.12: Schematic of the potential energy surfaces for the UV-induced photodissociation (green traces) and XUV-induced ionization (blue solid trace) processes. In the first step induced by the UV pulse, the potential energy of fragments with initial charges of $(q_1^i, q_2^i) = (0,0)$ or $(q_1^i, q_2^i) = (1,1)$ are shown (green dashed and green solid traces, respectively). In the second step induced by the XUV pulse, the potential energy of fragments with final charges of $(q_1^f, q_2^f) = (1,3)$ are shown (blue solid trace). The arrival-time of the XUV pulse is given by $t = \tau$ (grey dashed trace). The arrival of both UV and XUV pulses at the same time is given by $t = 0$. The red vertical line indicates the transfer of particles from the UV potential energy surface (green curve) to the XUV potential energy surfaces (blue curve).

to the initial charges of $(q_1^i, q_2^i) = (1,1)$. Consequently, their velocities increase as a function of time t , until the separation between the two charged fragments is large enough that no Coulomb force exists between the two fragments any more. In the most likely case of two neutral fragments, their potential energy remains constant at 0 (green dotted trace in Figure 8.12) since no Coulomb force is present between two particles with initial charges of $(q_1^i, q_2^i) = (0,0)$. Their velocities at time t remain constant and are equivalent to their initial velocities that is based on only the UV photodissociation process.

In the second process induced by the XUV pulse at $t = \tau$, the final positions and velocities from the first process (UV absorption) are used as the initial conditions in the numerical integration of the second process (XUV absorption) for particles with a final charge, q_1^f and q_2^f , in the time range of (τ, ∞) , referred to as Step 2 in Figure

8.12, as described by

$$\begin{aligned} \int_{t=\tau}^{t=\infty} \frac{dv}{dt} &= a \\ \int_{t=\tau}^{t=\infty} \frac{dx}{dt} &= v, \end{aligned} \tag{8.20}$$

where the particle trajectory is run until $t = \infty$. An increase in the separation distance between the two charge fragments also leads to a reduction in their potential energies (blue trace in Figure 8.12) since there is no Coulomb force between the two particles, as seen earlier for the first process with $(q_1^i, q_2^i) = (1,1)$. As mentioned earlier, the particles in the second process are flown until $t = \infty$ such that they approach their final velocities to obtain their asymptotic kinetic energies, which are the observable in the experimental measurements presented in this chapter.

In the case where $\tau = 0$ fs, the particles only propagate on the second potential energy surface (PES) to obtain the asymptotic energy corresponding to only the second process (ionization by the XUV pulse). To obtain an asymptotic energy that is characteristic of only the first process (dissociation induced by the UV pulse), the particles are propagated only along the first PES, with $\tau = \infty$. It should be noted that this method is only an approximation, and in reality the molecule dissociates along a complete potential energy surface. However, the good agreement seen between the simulated curve for the neutral dissociation of CH₃I and the corresponding experimental Coulomb channel shows that this is a valid approximation that can be used to characterize the neutral photodissociation dynamics in UV-XUV measurements.

The Coulomb curve provides a good handle on the t_0 in these measurements, which has an uncertainty of 50 fs due to the fitting of the simulated Coulomb curve to the corresponding experimental feature. Although the delay-dependent kinetic energy map for I³⁺ is much better resolved with the CCD camera, the PImMS1 camera can still resolve the $(0, x)$ and “intact” channels as well as certain aspects of the Coulomb channel.

The difference between the UV early and UV late ion images are presented in Figure 8.13. From these images, it is apparent that the low KER channel appears as a distinct

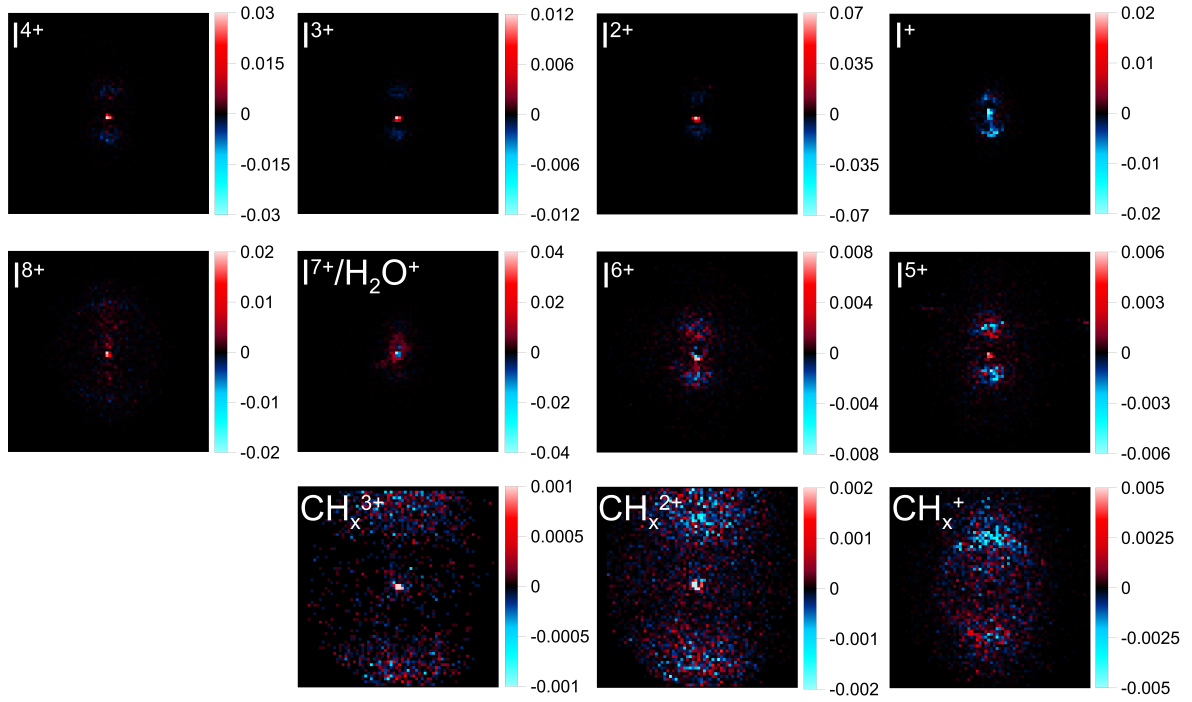


Figure 8.13: Difference ion images resulting after subtraction of the “UV late” from the “UV early” ion images for CH_3I shown in Figure 8.9. A positive (negative) intensity indicates an increase (decrease) in the ion yield.

central spot in the images for multiply charged iodine fragments, while a decrease in yield of the intact KER channel is observed at large radii for $\text{I}^+ - \text{I}^{5+}$. Both trends are due to the same reason given for the I^{3+} case earlier. A slight reduction in signal at higher KER is also observed in the carbon-containing fragments.

The delay-dependent kinetic energy maps for the iodine fragments are shown in Figure 8.14; these clearly contain a wealth of information. The simulated Coulomb curves for the neutral and charged dissociation cases are plotted in the maps for I^{3+} , I^{4+} , I^{5+} , and I^{6+} ions. The I^{5+} map in particular shows a distinct Coulomb channel for that clearly results from the neutral dissociation process since the shape and asymptotic energy of the experimental curve matches best with the simulated curve for the neutral dissociation (*i.e.* (0,0) to (1,5)) case.

The Coulomb channel is also present in the I^{3+} , I^{4+} and I^{6+} maps, which are best reproduced by the simulated Coulomb curves for neutral dissociation. Now that t_0 in these measurements is well defined from the simulation of the Coulomb channel, the focus of the analysis presented here shifts to the high “intact” and low (0, x) KER channels of iodine fragments from CH_3I . The projections of the former channel for

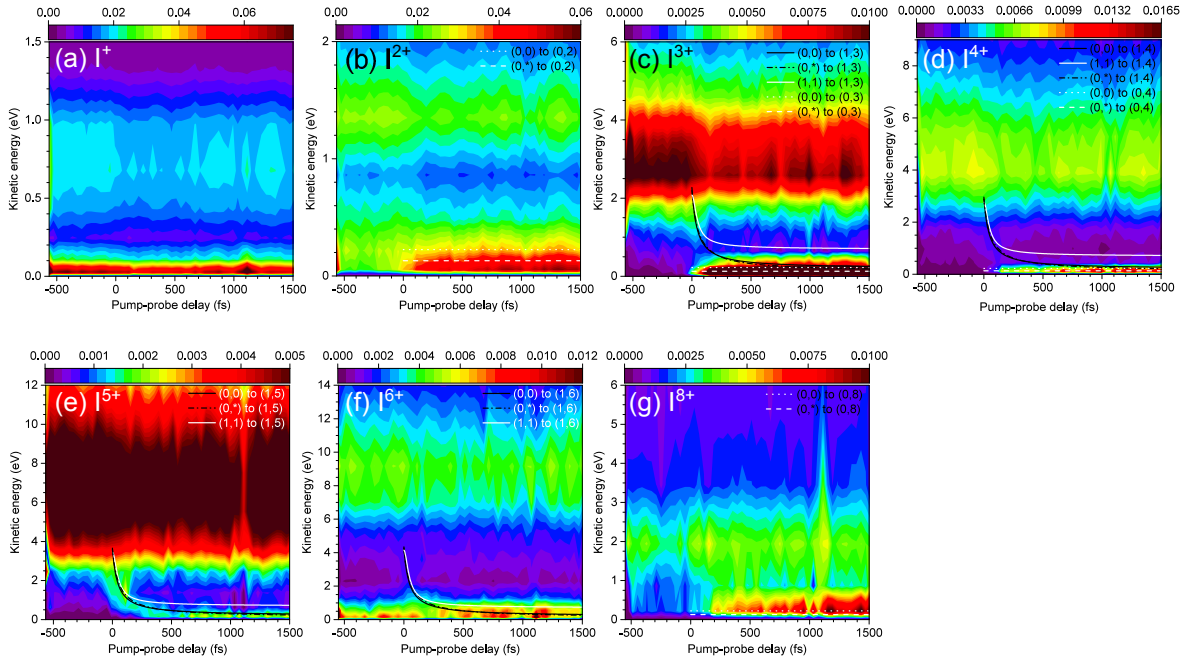


Figure 8.14: Maps of the delay-dependent kinetic-energy distributions are presented for ions formed from the UV-laser photodissociation and XUV-FEL ionization of 1D-aligned CH_3I simultaneously recorded with the PImMS1 camera. Specifically, maps for (a) I^+ , (b) I^{2+} , (c) I^{3+} , (d) I^{4+} , (e) I^{5+} , (f) I^{6+} and (g) I^{8+} ions are shown. The simulated Coulomb explosion simulation distributions for neutral (solid black traces) and charged (white solid trace) dissociation are shown in panels (c)-(f). In the neutral case, either I (black solid trace) or I^* (black dash-dot trace) fragments were used, while the charged dissociation case is shown for I^+ generated with zero initial velocity (white solid trace). The calculated kinetic energy of the $(0, x)$ channel for I (white dot trace) and I^* (white dash trace) are also shown. The data in each delay bin were normalised to the sum of the FEL pulse energy, and a jitter-correction was also applied as outlined in Ref. [84].

several iodine fragments are shown in Figure 8.15(a). A decrease in their yields is seen for all iodine fragments apart from I^{8+} , which occurs around t_0 and is indicative of a target depletion effect in which some of the molecules are removed by the UV laser pulse reducing the number of molecules available to interact with the XUV pulse. The time-dependent nature of the $(0, x)$ channel reveals information about the charge transfer process that occurs between multiply charged iodine fragments and their neutral co-fragment partner, details of which are discussed in the next section.

8.3.3 Charge Transfer

This section investigates the timescale of charge transfer after the UV-photodissociation and XUV-ionization of laser-aligned CH_3I molecules. Charge transfer is the movement

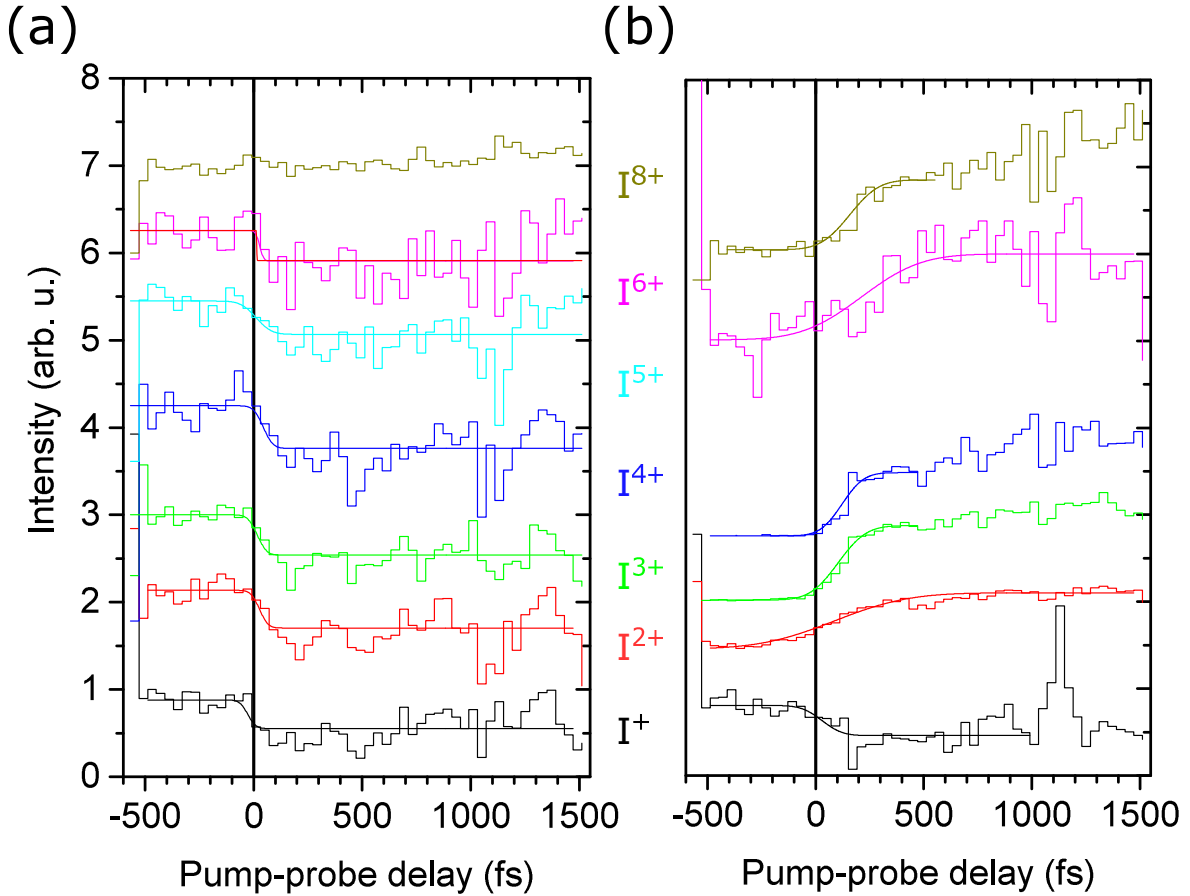
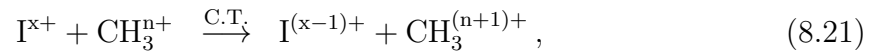


Figure 8.15: Projections of delay-dependent kinetic energy maps for CH_3I following the UV photodissociation and subsequent XUV inner-shell ionization of the molecule. The integrated yield of the (a) high and (b) low kinetic energy release (KER) channels are shown as a function of pump-probe delay in CH_3I . A Gaussian cumulative distribution function has been fitted to each KER channel.

of an electron from one particle to another as described by



for the case of CH_3I . The charge transfer dynamics between the multiply charged iodine, I^{x+} , and the neutral co-fragment, CH_3 , can be monitored by investigating the time-dependent nature of the $(0, x)$ KER channel [77, 81]. The projections of the $(0, x)$ channels in several iodine fragments are shown in Figure 8.15(b). A Gaussian cumulative distribution function has been fitted to each channel to extract the mid-point of the observed step-function, given by the mean of the CDF fit. This is taken as the onset of the channel, which is shown in Figure 8.16 for this work (red squares), with the errors taken as the fitting error of the Gaussian CDF fit. There is a very

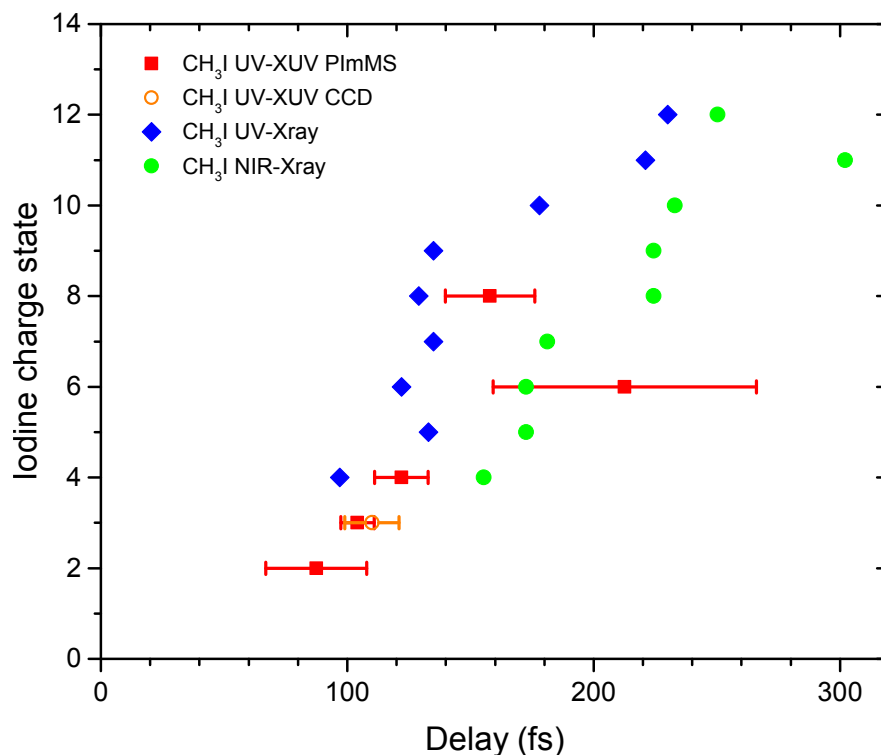


Figure 8.16: Onset times of the low $(0, x)$ KER channel for various charge states of iodine following the UV photodissociation and XUV inner-shell ionization of CH_3I , determined by the mean of a Gaussian cumulative distribution function fit. The mean CDF fit values are shown for this UV-XUV work (red squares), UV-Xray (blue diamonds) [81] and NIR-Xray (green circles) [77]. The corresponding value for I^{3+} recorded with the CCD camera from this work is also shown (orange circle). The error bars shown correspond to the fitting error of the Gaussian CDF fit.

good agreement between the values in this work (red squares) and previous work by Boll *et al.* in the UV-photodissociation of CH_3I (blue diamond) followed by soft X-ray ionization at the LCLS FEL facility [81]. However, the value corresponding to I^{6+} appears to be an outlier, which is unsurprising since the corresponding ion yield distribution was noisy. There is excellent agreement in the I^{3+} fragment recorded with both the PImMS1 (red square) and CCD (orange circle) cameras. A larger delay in the onset of the $(0, x)$ channel is present with increasing charge states of iodine due to the stronger polarizability of the charged iodine in attracting an electron away from its neutral co-fragment partner. Thus, charge transfer can occur over a larger distance (and hence time) with increasing charge states of iodine, leading to an increased delay in the onset of the $(0, x)$ channel [77, 81]. Above a certain distance (and hence time) charge transfer will cease as the two fragments are too far apart from each other for an electron to hop over from one particle to another [77, 81, 326–328].

8.3.4 Internuclear Distance of Fragments

The internuclear distance between two particles at the pump-probe delay, τ , at which the $(0, x)$ channel appears is described by [77, 81]

$$R(t) = R_{eq} + \tau \sqrt{\frac{2E_{kin}}{\mu}}, \quad (8.22)$$

where R_{eq} is the equilibrium bond distance, E_{kin} is the total asymptotic kinetic energy for the neutral dissociation of the molecule, and μ is the reduced mass given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \quad (8.23)$$

where m_1 and m_2 are the masses of the two particles. The internuclear distances extracted in this work (red squares) are in good agreement with those of UV-Xray (blue diamonds) [81] and NIR-Xray (green circles) [77] measurements, as shown in Figure 8.17. The internuclear distances in the UV cases were calculated using an equilibrium C-I bond distance of 220.0 pm [81] and an asymptotic total energy for the neutral dissociation to generate CH_3 and I^* of 1.286 eV [329]. The figure also shows that the appearance of the $(0, x)$ channel occurs at larger fragment distances with increasing charge state of iodine. This is a consequence of the iodine's ability to "steal" an electron away from the co-fragment. Again, the corresponding values for both the PImMS1 (red square) and CCD (orange circle) data in I^{3+} are in excellent agreement.

8.3.5 Over-The-Barrier Classical Model

The critical distance over which charge transfer is classically no longer permitted for fragments generated from a dissociating molecule is given, in atomic units, by [77, 326–328]

$$R_{\text{crit}}(q) = \frac{(p+1) + 2\sqrt{(p+1)q}}{E_i}, \quad (8.24)$$

where p and q are the charges of the two fragments, and E_i is the ionization energy of the radical co-fragment partner, which for the CH_3 radical is 9.86 eV [330]. The

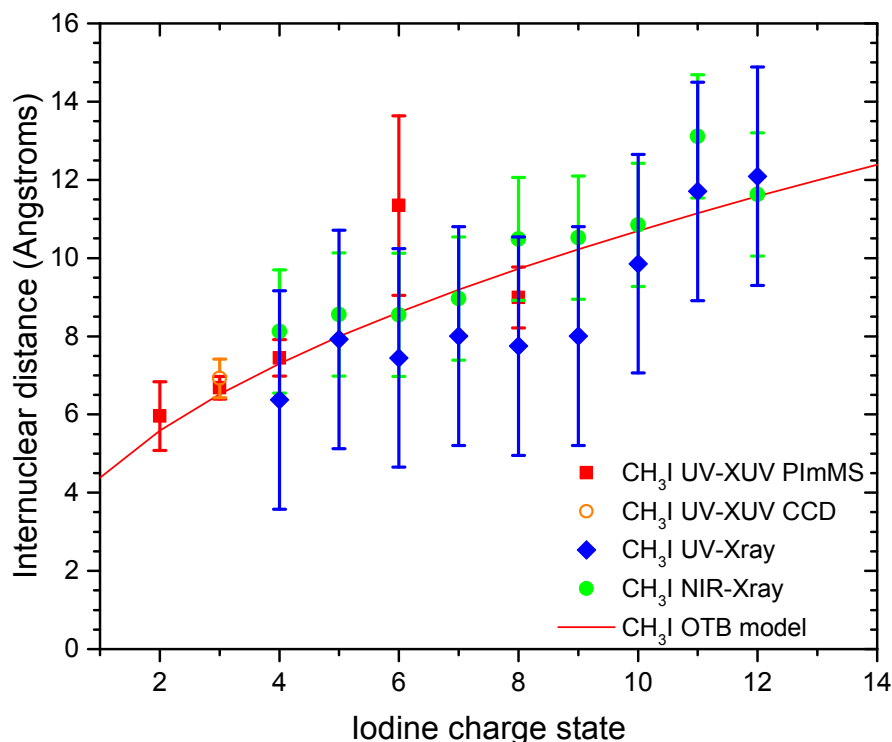


Figure 8.17: The internuclear distance in the onset of the $(0, x)$ KER channel for various charge states of iodine from CH_3I is shown for UV-XUV (red squares, this work), UV-Xray (blue diamonds) [81] and NIR-Xray (green circles) [77] measurements, as calculated using Equation (8.22). The corresponding value for I^{3+} recorded with the CCD camera from this work is also shown (orange circle). The critical distance calculated from the classical over-the-barrier model, using Equation (8.24), for CH_3I is shown as a solid red line.

experimentally obtained internuclear distances from this work (red squares) are in good agreement with the calculated critical distance (solid red line) as shown in Figure 8.17. The delay-dependent kinetic energy maps for carbon-containing fragments are shown in Figure 8.18(a)-(c), along with their corresponding integrated ion yields shown in panel (d). Significant noise exists in these distributions and so it is difficult to draw any meaningful conclusions about the time-dependent behaviour of the carbon-containing fragments from these measurements.

In the CH_3^+ map, a broad kinetic energy channel (5 eV - 11 eV) peaking at 8.8 eV is observed. Corrales *et al.* studied the Coulomb explosion of CH_3I with an intense ($I_0 \sim 1 \times 10^{13} \text{ W cm}^{-2}$) non-resonant 804 nm probe pulse at three intensities: 10, 30 and 60 TW cm^{-2} [131]. At the same intensity as the XUV pulse (30 TW cm^{-2}) used in the work presented in this chapter, Corrales *et al.* also measured a single broad total kinetic distribution peaking at 10.2 eV which corresponded to the Coulomb explosion of

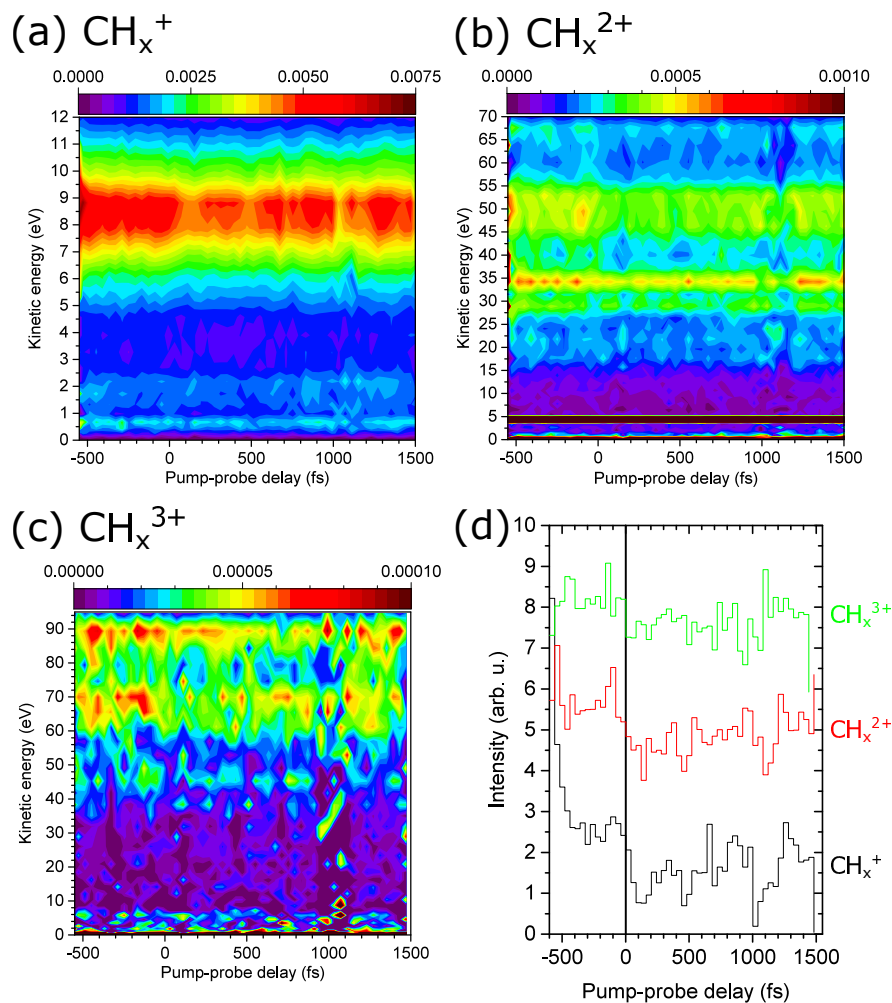


Figure 8.18: Maps of the delay-dependent kinetic-energy distributions are presented for (a) CH_x^+ , (b) CH_x^{2+} and (c) CH_x^{3+} ions formed from the UV-laser photodissociation and XUV-FEL ionization of 1D-aligned CH_3I . The data in each delay bin were normalised to the sum of the FEL pulse energy, and a jitter-correction was also applied as outlined in Ref. [84]. (d) The integrated ion yields of the high KER channels for the corresponding ions are shown. All data are recorded with the PImMS1 camera.

CH_3I^{3+} that generated the CH_3^+ and I^{2+} fragments [131]. The potential energy curves for the ground and excited states of CH_3I^{3+} were also simulated by Corrales *et al.*, which were shown to be repulsive in character (*i.e.* excitation by the 800 nm pulse lead to the rapid Coulomb explosion of CH_3I^{3+}) [131]. After accounting for conservation of momentum, Corrales *et al.* determined the mean kinetic energy of CH_3^+ fragments to be 8.96 eV which is in good agreement with the value of 8.82 eV from this work. In the I^{2+} map, as shown in Figure 8.14(b), the mean kinetic energy of the “intact” channel is 1.35 eV, which is in agreement with the value of 1.07 eV for I^{2+} from the (CH_3^+ , I^{2+}) Coulomb explosion channel measured by Corrales *et al* [131]. Thus, the “intact”

channel in the CH_3^+ map and the I^{2+} map corresponds to



In the CH_3^{2+} map, as shown in Figure 8.18(b), two “intact” channels appear at approximately 35 eV and 50 eV. The former corresponds to the $(\text{CH}_3^{2+}, \text{I}^{4+})$ Coulomb explosion channel, while the latter was difficult to assign and could correspond to either the $(\text{CH}_3^{2+}, \text{I}^{5+})$ and $(\text{CH}_3^{2+}, \text{I}^{6+})$ Coulomb channels. The “intact” channel in the I^{4+} map, as shown in Figure 8.14(d), appears at approximately 4 eV which also corresponds to the $(\text{CH}_3^{2+}, \text{I}^{4+})$ Coulomb channel. In the CH_3^{3+} map, as shown in Figure 8.18(c), the “intact” channel between 60–95 eV corresponds to the generation of CH_3^{3+} with I^{5+} , I^{6+} , and I^{7+} fragments. In the I^{5+} and I^{6+} maps (panels e and d in Figure 8.14), the mean kinetic energy release of the “intact” channels appear at 6.5 eV and 8.0 eV, respectively, which correspond to the CH_3^{2+} and CH_3^{3+} co-fragment partners for both charge states of iodine. In the I^+ map, as shown in Figure 8.14(a), the “intact” channel appears at 0.68 eV, which corresponds to the $(\text{CH}_3^+, \text{I}^+)$ Coulomb channel.

This section has demonstrated the capability of the PImMS1 camera in recording all ions simultaneously for a like-for-like comparison between fragments generated from the proof-of-principle experiment of UV-induced dissociation and XUV-ionization of laser-aligned CH_3I . In the following section, the studies are extended to 2,6-difluoroiodobenzene to investigate the photodissociation and charge dynamics of a more complex molecule.

8.4 Photodissociation of DFIB and Subsequent Inner-Shell Ionization

This section investigates the photodissociation and charge transfer dynamics of laser-aligned 2,6-difluoriodobenzene (DFIB) molecules following their UV-induced dissociation by a Ti:Sa laser pulse and subsequent ionization by an XUV FEL pulse. The photodissociation dynamics were investigated using both a CCD camera and the PImMS1 time-stamping camera. The latter was used to study charge transfer within the molecule, by comparing the timescales for the various KER channels of the simultaneously recorded fragments.

The ToF traces corresponding to UV early (red solid line) and UV late (black solid line) delays are shown in Figure 8.19 for 1D-aligned DFIB molecules. Ion images for the corresponding ToF peaks shaded in grey are shown above the ToF spectrum for both delays. As seen in Section 8.3.1 in the case of CH_3I , a central spot appears in the ion images for multiply charged iodine fragments at UV early delays that is characteristic of the UV-induced dissociation of the carbon-iodine bond. A decrease in the yield of CH_x^+ , CH_x^{2+} and F^+ ions is also seen at UV early delays, and is indicative of charge transfer between a multiply charged iodine fragment and its co-fragment partner.

The molecule remains intact in the absence of the UV pulse; whilst ionization by the XUV pulse can generate a multiply charged iodine fragment with a neutral carbon-containing co-fragment. However, since the co-fragment is in close proximity to the highly charged iodine ion, an electron can hop over from the former to the latter [77, 81]. In the presence of the UV pulse, the carbon-iodine bond is broken and a free iodine atom is generated which is no longer in close proximity to its co-fragment. Thus, charge transfer will cease and significantly more co-fragments will remain neutral, leading to a reduction in the corresponding co-fragment ion yield.

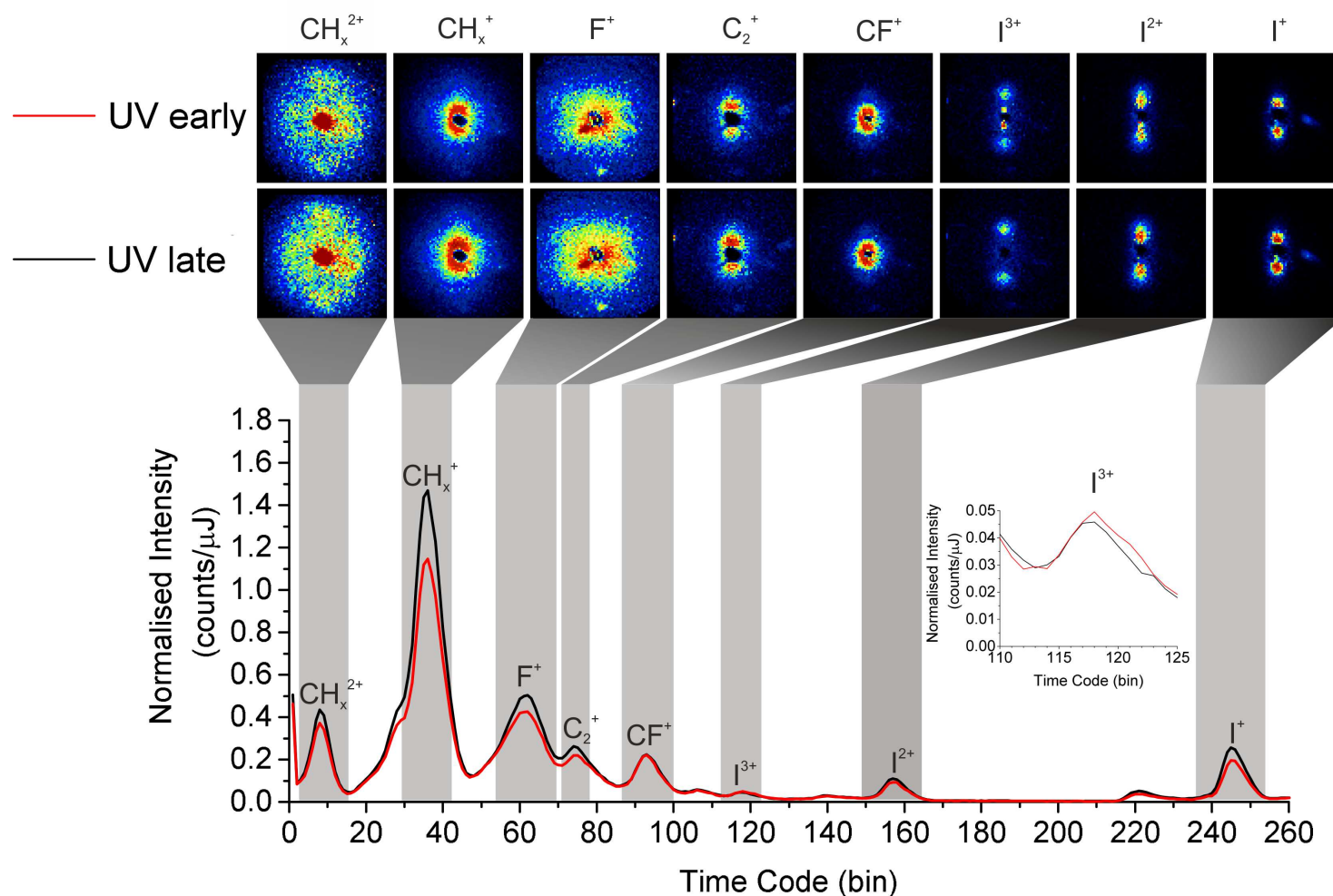


Figure 8.19: Time-of-flight spectrum of ions formed after the absorption of UV photon(s) either before (UV early, red solid line) or after (UV late, black solid line) the absorption of XUV photons by 1D-aligned DFIB molecules. Assignments for each peak are shown in the figure, with the corresponding ion images for the shaded grey ToF peaks shown above the ToF spectrum. The inset shows a close-up of the I^{3+} ToF profile for both UV early and late delays. All data are recorded with the PImMS1 camera.

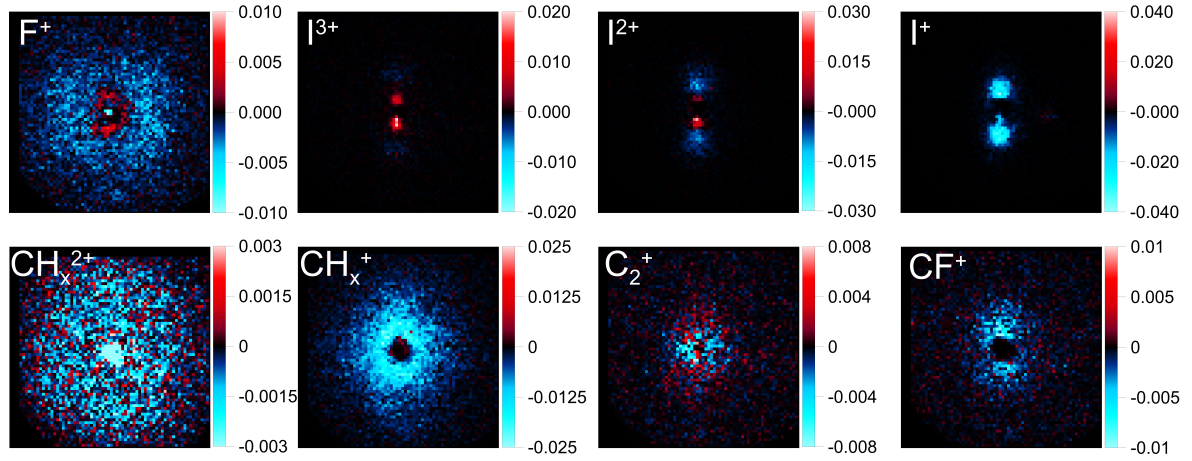


Figure 8.20: Ion images obtained after subtraction of the “UV late” from the “UV early” images shown in Figure 8.19. A positive (negative) intensity indicates an increase (decrease) in the yield.

The difference between the “UV early” and “UV late” ion images are shown in Figure 8.20 with red and blue indicating increase and reduction in intensity, respectively. The decrease in intensity seen for the “intact” high KER channel of the iodine fragments may be due to either target depletion or charge transfer depending on the time evolution nature of the signal. In the presence of the UV pulse, a low KER channel clearly appears in the centre of the difference images for multiply charged iodine fragments due to photodissociation, as discussed above. A decrease in signal is seen in CH_x^+ , CH_x^{2+} , CF^+ and C_2^+ ions for the same reason as given for the high KER channel of iodine - either target depletion or charge transfer. In F^+ , an increase and decrease in yield is seen in the low and high KER channels, respectively, with the latter due to either charge transfer or target depletion. The reason for the former is still unclear, but may be due to contamination with background signal (such as H_2O^+ ions). The next section focuses on the time-resolved kinetic energy maps for I^{3+} and I^{2+} , since these show the clearest time-dependent effects.

8.4.1 Dissociation of DFIB

The high-resolution delay-dependent kinetic energy maps of I^{3+} and I^{2+} recorded with a CCD camera and time-gated over their respective ToF profiles are shown in Figures 8.21 and 8.22. From these maps, up to four time-dependent features are visible: the

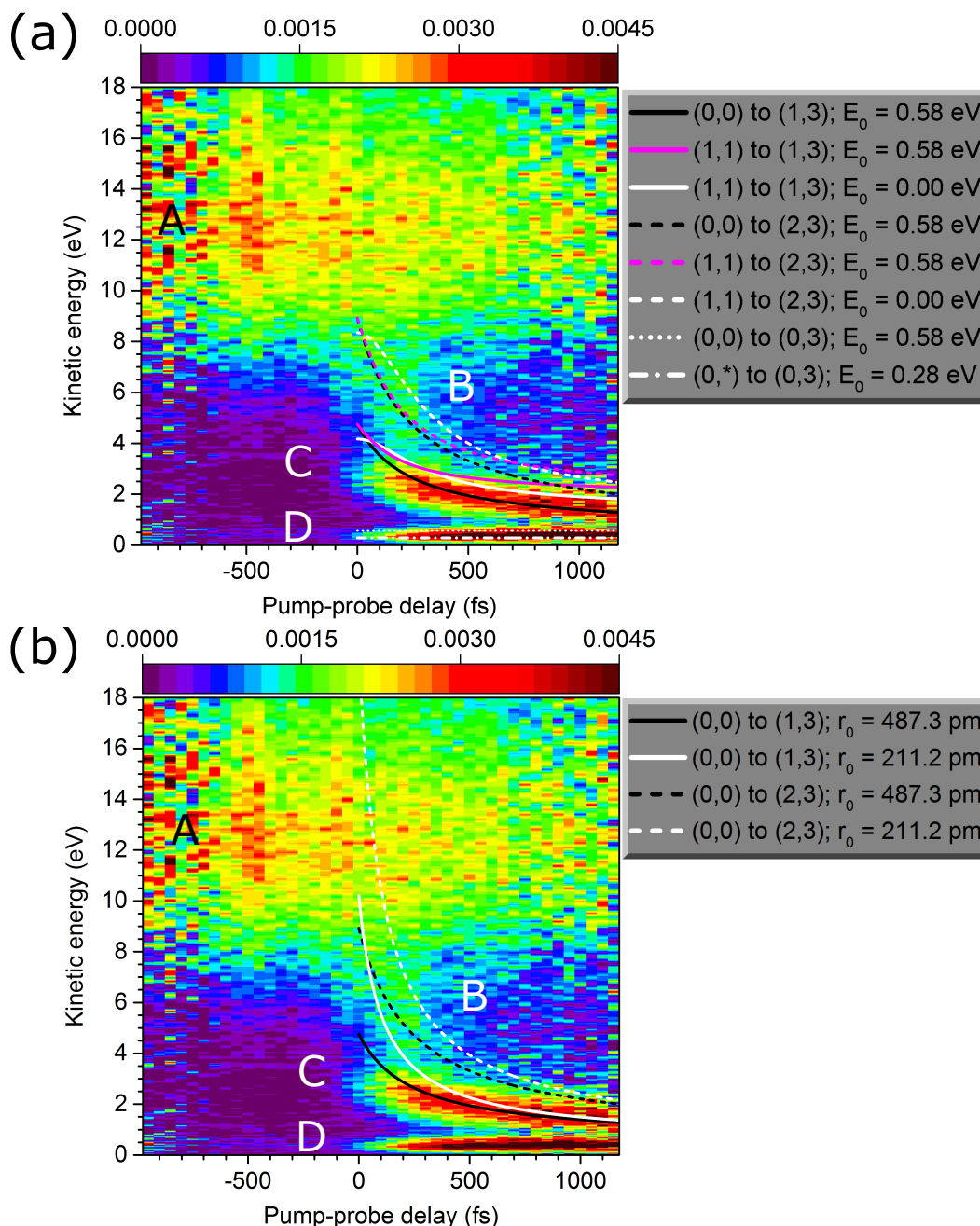


Figure 8.21: High-resolution delay-dependent kinetic-energy maps of I^{3+} after the UV-laser photodissociation and XUV-FEL ionization of 1D-aligned DFIB recorded with a conventional CCD camera. Four KER distributions are visible: (A) Intact molecule, (B) high energy Coulomb curve, (C) low energy Coulomb curve, and (D) the $(0,x)$ neutral channel. Panel (a) shows the simulated Coulomb curves for the neutral dissociation (black traces) of 2,6-DFIB. The simulated curves for the charged dissociation case is also shown where I^+ was generated with an initial kinetic energy of either 0.00 eV (white solid or dashed traces) or 0.58 eV (magenta solid or dashed traces). The calculated kinetic energy of the $(0,x)$ channel for I (white dot trace) and I^* (white dash-dot trace) are also shown. Panel (b) shows the simulated Coulomb curves for the neutral dissociation of DFIB with an equilibrium distance of 491 pm (black traces) and 211.2 pm (white traces). Experimental data shown in this figure was pulse energy and BAM corrected by Evgeny Savelyev.

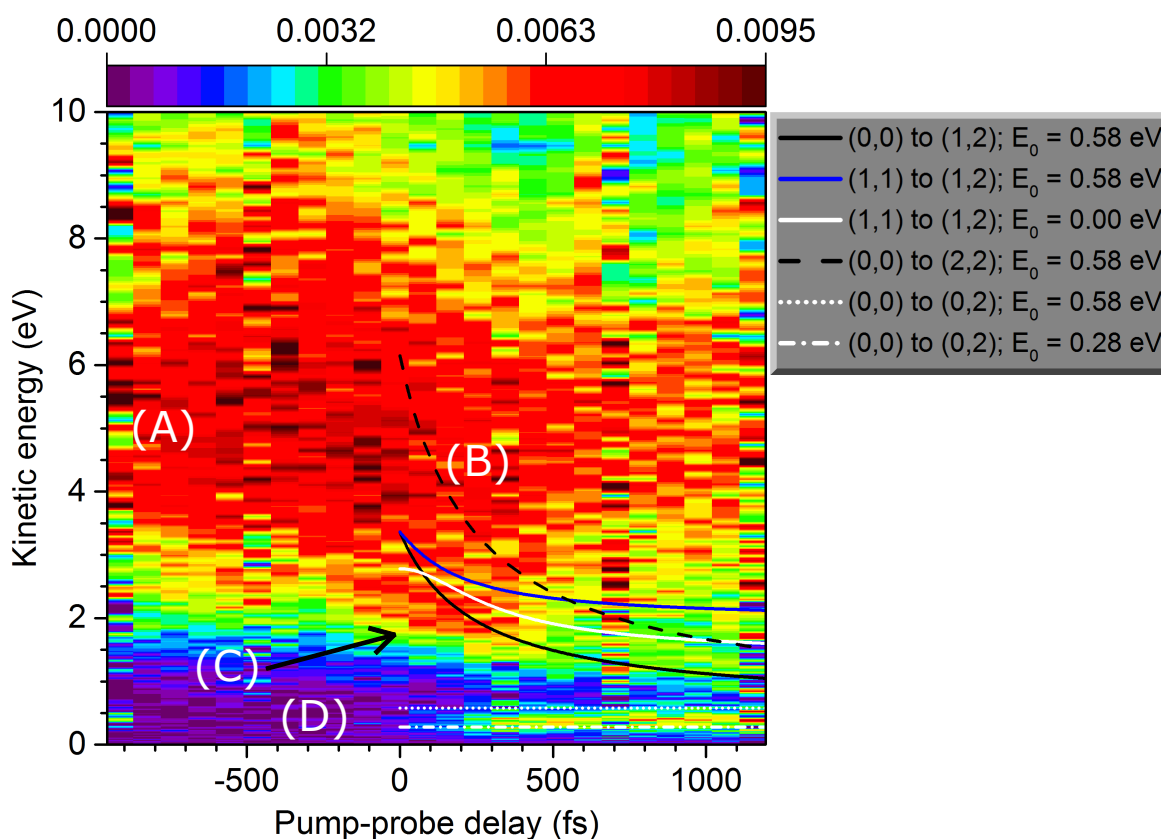


Figure 8.22: High-resolution delay-dependent kinetic-energy maps of I^{2+} after the UV-laser photodissociation and XUV-FEL ionization of 1D-aligned DFIB were recorded with a conventional CCD camera. Four KER distributions are labelled: (A) “intact” molecule channel, (B) high energy Coulomb channel, (C) low energy Coulomb channel, and (D) the $(0, x)$ neutral channel. The simulated Coulomb curves for the neutral dissociation (black traces) are shown, while the charged dissociation case is shown for I^+ generated with an initial kinetic energy of either 0.00 eV (white solid trace) or 0.58 eV (blue solid trace). The calculated kinetic energy of the $(0, x)$ channel for I (white dot trace) and I^* (white dash-dot trace) are also shown. Experimental data shown in this figure was pulse energy and BAM corrected by Evgeny Savelyev.

“intact” channel (feature A), two Coulomb channels (features B and C), and the $(0, x)$ channel (feature D). Figure 8.23 shows the kinetic energy distributions for I^{3+} and I^{2+} which were extracted by integrating the delay-dependent kinetic energy maps shown in Figures 8.21 and 8.22, respectively, across all pump-probe delays. A Gaussian fit was applied to the $(0, x)$ channels in both ions and the centre of the Gaussian distribution was determined to be 0.38 ± 0.12 eV and 0.37 ± 0.13 eV for I^{3+} and I^{2+} , respectively. It should be noted that the ion images corresponding to the delay-dependent maps were not pBasex-inverted since the very low KER $(0, x)$ channel was masked by artefacts and noise that are introduced by the inversion program.

The photodissociation of 3,5-difluoriodobenzene at 267 nm has been previously

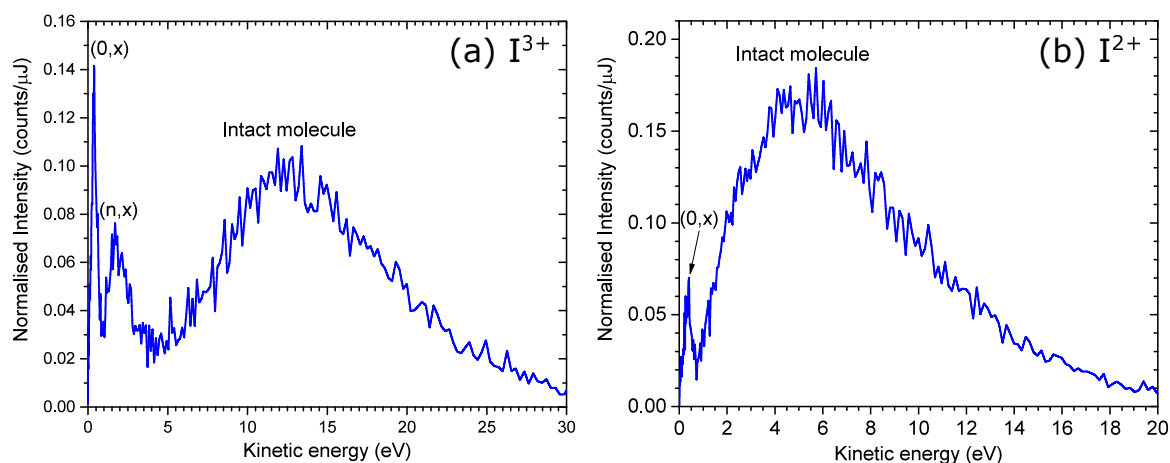


Figure 8.23: The kinetic energy distribution of the (a) I^{3+} and (b) I^{2+} ion fragments generated after the UV-laser photodissociation and XUV-FEL ionization of 1D-aligned DFIB. The distributions have been obtained from integration along all pump-probe delays from the corresponding maps recorded by the CCD camera. Each KER channel is annotated in the figure. The (n, x) channel refers to the ejection of I^{x+} with DFB^{n+} .

studied by Murdock *et al.* [22]. In their study, they measured a total kinetic energy release of 1.15 eV and 0.71 eV for the $(DFB + I)$ and $(DFB + I^*)$ products, respectively. Accounting for conservation of momentum, the iodine fragments were calculated to be ejected with kinetic energies of 0.54 eV and 0.33 eV, respectively. The kinetic energy of iodine in this work (~ 0.38 eV) is in close agreement with that of I^* measured by Murdock *et al.* (0.33 eV) [22]. Therefore, the majority of iodine fragments generated by the UV pulse in this work is in its spin-orbit excited state, I^* .

As shown for CH_3I in Section 8.3.2, the kinetic energy release of the iodine fragment can be calculated from the UV photon energy, $E_{h\nu}$, if the dissociation energy, D_0 , is known. As there is no previously reported D_0 value for 2,6-DFIB, the corresponding value for 3,5-DFIB molecule (2.89 eV [22]) was used in the following calculations. Since one 267 nm photon (4.65 eV) is used to resonantly dissociate the molecule, an energy of 1.76 eV is available to the I and DFB fragments. The fraction of the total available energy transferred into translational energy, f_T , in iodobenzene at 267 nm was determined by Lin *et al.* [331] to be 0.70 and 0.82 for I and I^* , respectively. This is in good agreement with earlier measurements carried out by El-Sayed and coworkers [332] who obtained corresponding values of 0.76 and 0.82 at 304 nm. The same group also re-

ported f_T values of 0.56 and 0.20 for I and I*, respectively, from pentafluoroiodobenzene at the same wavelength [333].

In the simulation of 2,6-DFIB, the f_T value of 0.70 were used for both I and I*, which was based on the values of f_T reported by previous works for I and I* discussed above. This leads to a calculated KER of 0.58 eV for the I fragment. For the I* fragment, the spin-orbit splitting in iodine is 0.943 eV [15], and the KER is calculated to be 0.28 eV. The calculated KER values for I (white short-dot line) and I* (white dash-dot line) are shown in the delay-dependent maps for both I²⁺ and I³⁺, with the calculated KER values clearly capturing the minimum and maximum KER value of the experimental (0, x) dissociation channel (feature D in Figure 8.21). A closer investigation of the delay-dependent KER channels is now given.

The t_0 in these measurements was determined by fitting the simulated Coulomb curves to the experimental features B and C in Figure 8.21 using the same methodology as for CH₃I. In panel (a), the very intense Coulomb curve (feature C) is best characterized by the simulated Coulomb curve from the (0,0) to (1,3) neutral dissociation of DFIB. The (1,1) to (1,3) charged cases where the I⁺ ion is generated with an initial kinetic energy of either 0.58 eV (magenta solid line) or 0.00 eV (white solid line) both approach an asymptotic energy that is much higher than seen experimentally in feature C. The slight “curvature” seen in the first 100 fs of the stationary charged dissociation case (white dashed trace) is due to the two relatively heavy fragments taking some time to gain kinetic energy in order to separate away from each other. Thus, the experimental feature C is assigned as the (0,0) to (1,3) channel.

The assignment of the weaker Coulomb curve (feature B) is more difficult as the high energy part of the experimental curve (<300 fs) can be simulated by both the neutral and charged dissociation cases that generate an iodine fragment with an initial kinetic energy of 0.58 eV. The charged dissociation case where both charged fragments have zero initial velocity shows the worst agreement with the experimental feature, and so this simulated curve can be ruled out. Since the very intense Coulomb channel (feature C) was generated through neutral dissociation, the same must also be true for the weaker Coulomb channel (feature B). Thus, the weaker Coulomb channel is

assigned as the (0,0) to (2,3) neutral dissociation case.

Panel (b) shows the simulated Coulomb curves for the neutral dissociation of DFIB at an equilibrium separation, R_{eq} , of 491 pm [291] (black traces) and 211.2 pm [22] (white traces). The former corresponds to the distance between the iodine atom and the furthest away carbon on the benzene ring, and has been shown to best agree with the experimentally determined kinetic energy release of the $\text{I}^+ + \text{DFB}^+$ channel obtained from an electron-ion-ion coincidence experiment performed with synchrotron radiation at 107 eV [291].

The second value (211.2 pm) corresponds to the distance between the iodine atom and the closest carbon on the benzene ring, and was taken from the calculated value for 3,5-DFIB by Murdock *et al.* [22]. Both experimental features B and C are well characterized by the fits with an equilibrium distance of 491 pm (black traces), while much larger kinetic energies are generated at 211.2 pm due to the much smaller separation between fragments and hence a stronger Coulombic repulsion. As such, the charge on the benzene ring is placed as far away as possible from the charged iodine, as seen in the electron-ion-ion coincidence measurements performed on the static ionization of the same molecule [291].

The Coulomb channels in I^{3+} are much more pronounced for DFIB than they were for CH_3I because the DFB fragment from DFIB has a large total absorption cross-section at 107 eV when compared to the CH_3 fragment from CH_3I . Thus, DFB is much more likely to emit an electron from the molecular valence shell to generate a singly charged ion than in the case of CH_3 . Since we are operating in the multi-photon XUV regime with the FLASH FEL, I^{3+} ions can also be ejected with DFB^{2+} (see Chapter 7). The difference in photoionization cross-sections is also observed due to the presence of a single Coulomb channel in the case of CH_3I , which corresponds to the emission of I^{3+} with CH_3^+ only. In contrast, two Coulomb channels are accessible in the DFIB case corresponding correspond to a singly and a double charged co-fragment, DFB^+ and DFB^{2+} .

The I^{2+} map in Figure 8.22 shows the appearance of a Coulomb channel over small, positive delays above which it disappears. As observed for CH_3I , this is indicative of

charge transfer in the molecule, characterized by the delayed onset of the $(0, x)$ channel (feature D in 8.22). The $(0, x)$ channel of I^{3+} in DFIB (feature D in Figure 8.21) also appears with a delayed onset, where charge transfer occurs from the $(0, 3)$ channel to generate the $(1, 2)$ channel. This leads to the appearance of a $(1, 2)$ Coulomb channel in the I^{2+} map, shown in Figure 8.22 as feature C, in the presence of the UV pulse for a period of time that is dictated by the charge transfer process in the $(0, 3)$ channel. At large positive delays where the $(0, 3)$ channel in I^{3+} is no longer depleted, the process of charge transfer will have ceased, leading to the disappearance of the $(1, 2)$ channel which is seen in the I^{2+} map at times greater than 400 fs.

Although the Coulomb channel in I^{2+} (feature C) is not as distinct as for the I^{3+} ion, the simulated Coulomb curve from the neutral dissociation case also best matches the experimental Coulomb channel in I^{2+} (feature C in Figure 8.22). The likelihood of generating two charged fragments is already very low due to the low intensity of the UV pulse used in these measurements. Furthermore, the I^+ fragments generated with an initial kinetic energy of 0.58 eV by the UV pulse have an asymptotic energy that is much higher than the experimental Coulomb curve. The appearance of the Coulomb channel (feature C) in I^{2+} only in the presence of the UV pulse, and its subsequent disappearance around the time that charge transfer between I^{3+} and DFB ceases, indicates that this channel is a direct result of the charge transfer process that occurs in the $(0, 0)$ to $(0, 3)$ channel.

Interestingly in I^{3+} , the $(1, 1)$ to $(1, 3)$ Coulomb channel has the same delayed onset as the $(0, 0)$ to $(0, 3)$ channel. This suggests that charge transfer also occurs with the $(1, 3)$ Coulomb channel to generate I^{2+} with DFB^{2+} and possibly DFB^{3+} depending on the number of electrons involved. This coincides with a decrease in yield of the “intact” channel (~ 6 eV) in I^{2+} , and the kinetic energies that I^{2+} is ejected with imply that its co-fragment must be multiply charged (*i.e.* DFB^{2+} and/or DFB^{3+}) assuming that the equilibrium distance is 491 pm [291]. Thus, we have qualitatively shown that signatures of charge transfer associated with the I^{3+} ion appear in both I^{3+} and I^{2+} maps. The $(0, x)$ channel in I^{2+} also has a delayed onset time where charge transfer occurs with I^{2+} and DFB to generate I^+ and DFB^+ . In the next section, the PImMS1 camera is

used to extract time constants associated with several KER channels in various ions generated by the UV and XUV pulses that allows for a like-for-like comparison and investigation of charge transfer dynamics in the DFIB molecule.

8.4.2 Charge Transfer Dynamics

The delay-dependent kinetic energy maps recorded with the PImMS1 camera are shown in Figure 8.24 for (a) I^{3+} , (b) I^{2+} , (c) I^{+} , and (d) F^{+} ions. The data agrees well with the correspond CCD data. In the multiply charged iodine fragments the simulated Coulomb curves are shown for the (0,0) to (1, x) and (0,0) to (2, x) channels. In the I^{3+} map, the same two Coulomb channels are seen in the PImMS1 data as the CCD data, although they are not as well resolved. The simulated Coulomb curves match the experimental features B and C, which gave a good handle on the t_0 of these measurements, although a fitting uncertainty of ~ 50 fs does exist.

In the I^{2+} ion, the intense short-lived Coulomb feature that appeared in the CCD camera also appears in the corresponding PImMS1 data, with the extremes of this Coulomb channel captured by the (0,0) to (1,2) and (0,0) to (2,2) simulated curves, as shown in Figure 8.24(b). The disappearance of this Coulomb channel in the I^{2+} map (feature C) also coincides with the appearance of the (0, x) channel in the I^{3+} map (feature D), as also observed in the CCD data. The depletion in the yield of the intact high KER channel in I^{2+} is also seen in the PImMS1 data. The I^{+} map, shown in panel (c), shows target depletion beginning around t_0 at all kinetic energies of I^{+} . In the F^{+} map, shown in panel (d), there is a decrease in the yield of the high KER channel accompanied by an increase in yield of the low KER channel. The former may be due to charge transfer, while the latter may be a target depletion effect.

Figure 8.25 shows the integrated ion yields for the most relevant KER channels in I^{+} , I^{2+} , I^{3+} and F^{+} ions. Gaussian fits were applied to the ion yield distributions to extract time constants. As shown in CH_3I earlier, the mid-point of the rise or fall in ion yield is taken as the centre of the Gaussian fit. In the (0, x) channel (~ 0.3 eV, gold trace) of I^{3+} , the step function rises at 221 ± 13 fs and coincides with the step-function fall in the “intact” high KER channel (~ 7 eV, pink trace) of the I^{2+} ion at

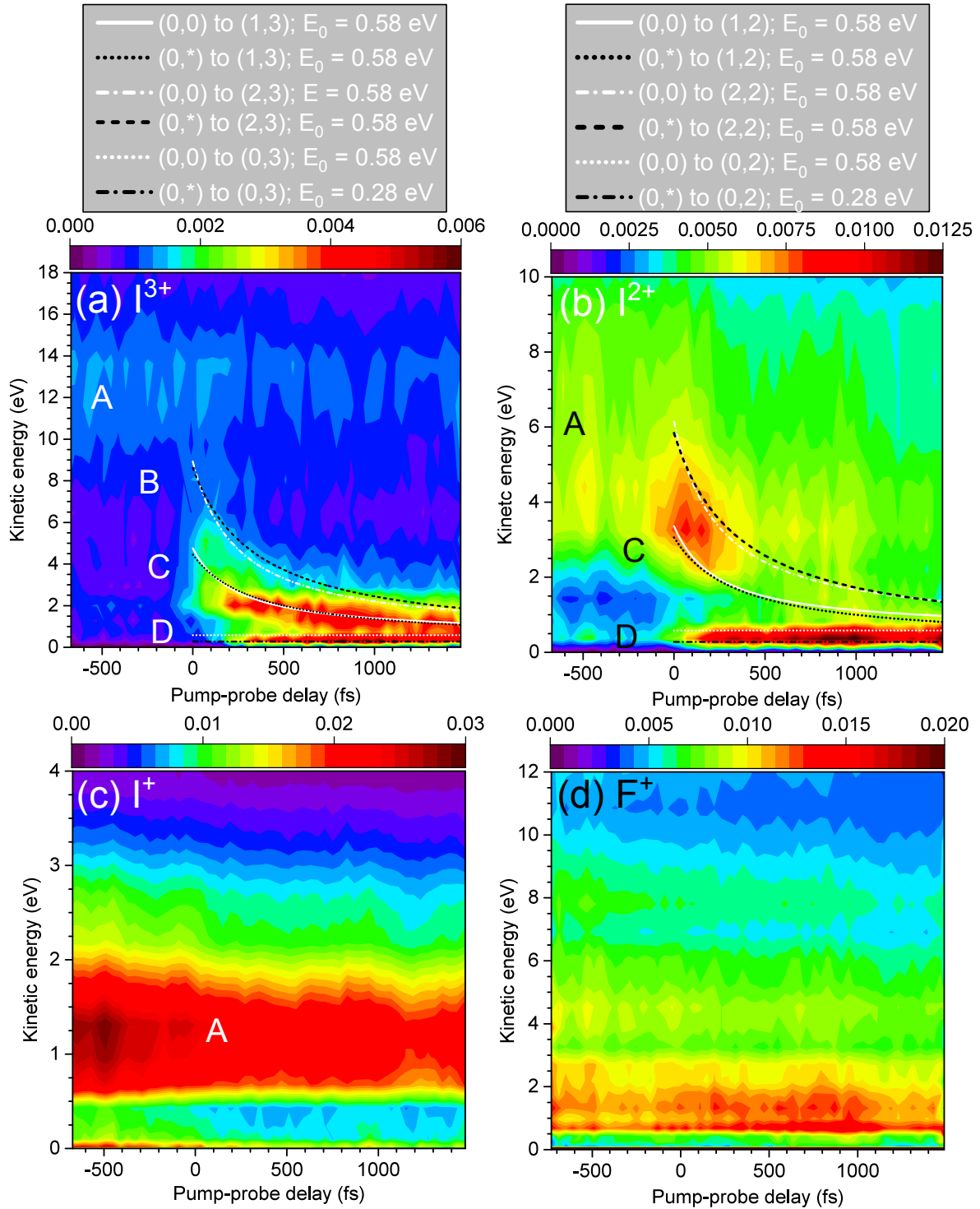


Figure 8.24: Maps of the delay-dependent kinetic-energy distributions of (a) I^{3+} , (b) I^{2+} , (c) I^+ , and F^+ ions are presented following the UV-laser photodissociation and XUV-FEL ionization of 1D-aligned DFIB recorded with the PImMS1 camera. Up to four KER channels exist in I^{3+} and I^{2+} ions, which are the: (A) “intact” channel, (B) weak Coulomb channel, (C) strong Coulomb channel, and (D) $(0,x)$ channel. The legends for both I^{2+} and I^{3+} are shown above their corresponding maps. The simulated KER distributions are shown for I (black traces) and I^* (white traces). The data in each delay bin were normalised to the sum of the FEL pulse energy, and a jitter-correction was also applied as outlined in Ref. [84].

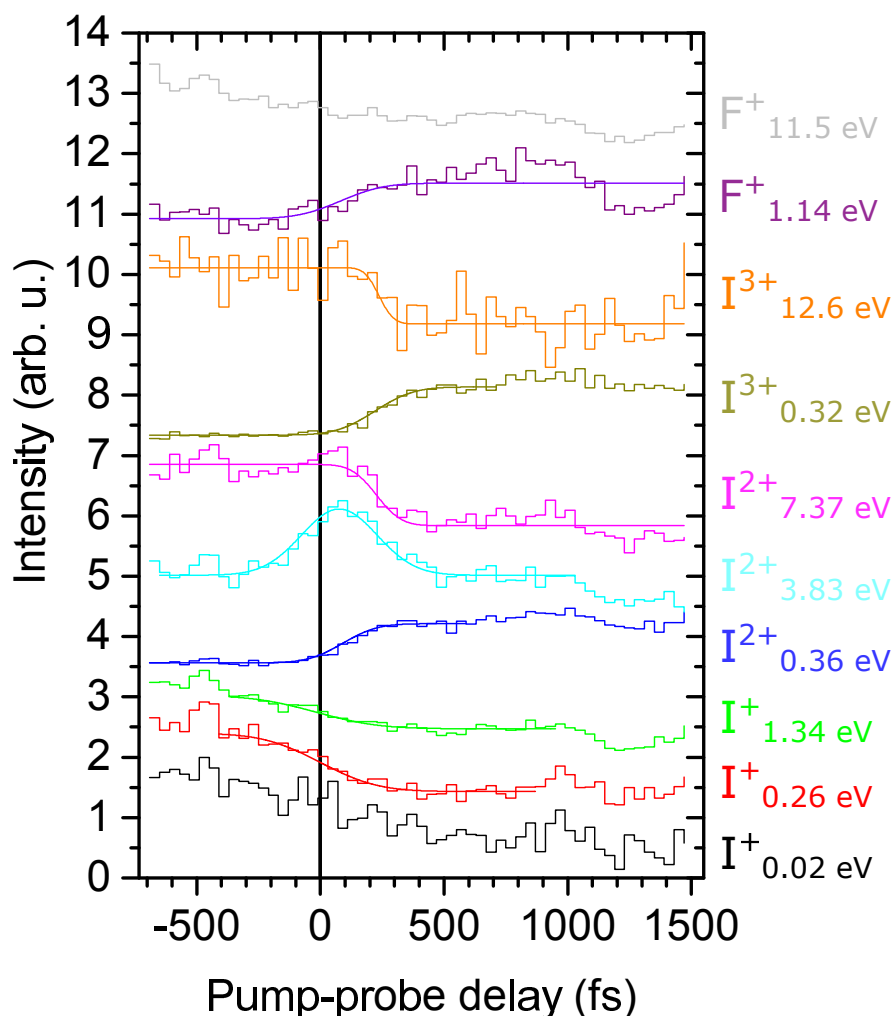


Figure 8.25: Projections of delay-dependent kinetic energy maps for DFIB is presented, for certain KER ranges, following the UV photodissociation and subsequent XUV inner-shell ionization of the molecule recorded with the PImMS1 camera. The integrated yield of the low, medium and high KER channels of the I^+ , I^{2+} , I^{3+} , and F^+ ions as a function of pump-probe delay in DFIB are shown. A Gaussian cumulative distribution function has been fitted to each KER channel where possible.

227 ± 20 fs. The short-lived Coulomb channel in I^{2+} (~ 4 eV, cyan trace) was fitted using a Gaussian distribution with a centre of 76 ± 10 fs, and the decrease in this Gaussian distribution coincided with the rise (fall) of the $(0, x)$ channel (“intact” channel). The time-evolution of these three channels in both I^{2+} and I^{3+} maps indicate that charge transfer occurs between I^{3+} and neutral DFB to generate I^{2+} and DFB^+ fragments.

In I^{2+} , a step-function rise in the $(0, x)$ channel (~ 0.4 eV, blue trace) appears at 91 ± 12 fs, with a delayed onset due to charge transfer from $(I^{2+} + DFB)$ to $(I^+ + DFB^+)$ products. In the I^+ data, a step-function depletion in two KER channels (~ 0.3 and 1.3 eV, red and green traces, respectively) are seen that appear at 0 ± 27 fs and

-18 ± 42 fs. Since they disappear around t_0 , these two channels are assigned to target depletion. Due to high noise levels, a fit could not be applied to the very low KER channel of I^+ (~ 0.02 eV, black trace).

It should also be noted that in the I^{3+} ion, a step-function fall in yield is seen for the intact high KER channel appearing at 237 ± 29 fs, which is indicative of charge transfer from I^{4+} and DFB, although I^{4+} was not resolved in these measurements. The low KER channel of F^+ (~ 1.1 eV, purple trace) appears at 82 ± 68 fs. This rise in yield coincides with the dissociation of the C-I bond and the loss of a free iodine atom, and could lead to the fragmentation of the DFB radical that generates low KER F^+ ions. No fit could be applied to the high KER channel of F^+ (~ 12 eV, grey trace), although a small decrease in yield appears to be present around t_0 which is most likely a target depletion effect.

The delay-dependent maps and ion yields of the carbon fragments are presented in Figure 8.26 for (a) CH_x^{2+} , (b) CH_x^+ , (c) C_2^+ and (d) CF^+ ions. In the CH_x^+ ion, a step-function fall in yield is observed in the various KER channels present in panel

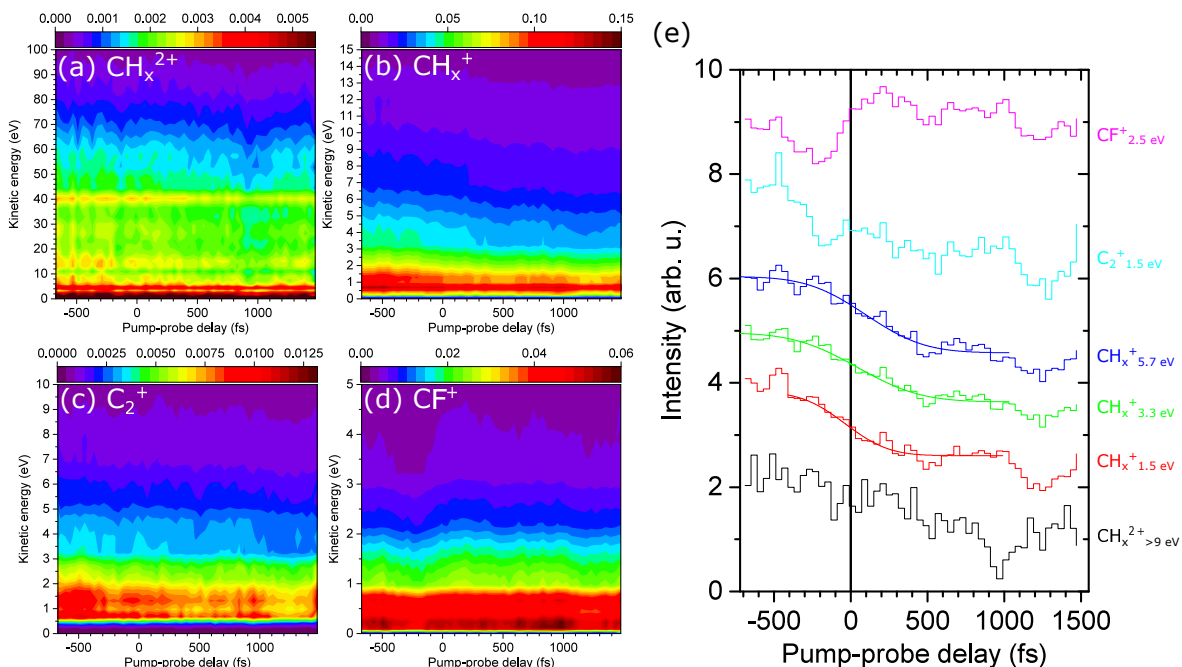


Figure 8.26: The delay-dependent kinetic-energy maps for (a) CH_x^{2+} , (b) CH_x^+ , (c) C_2^+ , and (d) CF^+ ions are presented from DFIB. (e) Projections of delay-dependent kinetic energy maps for these fragments are also presented, for the high KER range, following the UV photodissociation and subsequent XUV inner-shell ionization of DFIB. A Gaussian cumulative distribution function has been fitted to each KER channel where possible. All data are recorded with the PImMS1 camera.

(e). The low KER channel (~ 1.5 eV, red trace) appears at -37 ± 41 fs and is due to target depletion since it occurs around t_0 , and its kinetic energy release suggests that CH_x^+ in this channel is most likely ejected with an I^+ ion partner. A small delay in the disappearance of the medium KER channel (~ 3.3 eV, green trace) at 42 ± 33 fs suggests that a small degree of charge transfer is occurring with its I^{2+} ion partner. The high KER channel (~ 5.7 eV, blue trace) suggests simultaneous ejection with either I^{3+} or I^{4+} , with a delayed disappearance at 97 ± 34 fs suggestive of charge transfer. The CH_x^{2+} , CF^+ , and C_2^+ distributions could not be fitted satisfactorily, although in the latter a qualitative decrease in the ion yield is seen at around t_0 and is most likely due to target depletion.

The onset of the $(0, x)$ channel in multiply charged iodine fragments for DFIB (black stars) and CH_3I (red squares), recorded with the PImMS1 camera, are shown in Figure 8.27(a). The available CCD camera data for DFIB (cyan circles) and CH_3I (orange circle) are also plotted. As seen earlier for CH_3I , the corresponding PImMS1 and CCD data also agree very well with each other in the DFIB data. The I^{3+} ion from DFIB appears at a much larger delay than in CH_3I since it contains a much heavier co-fragment, DFB. Thus, the dissociation process occurs on a longer timescale in DFIB, and so charge transfer between I^{3+} and DFB can occur within a longer period of time and ultimately lead to a larger delay in the onset of the $(0, x)$ channel in I^{3+} than in the case of CH_3I . A small discrepancy is seen in the PImMS1 and CCD data corresponding to the I^{2+} ion from DFIB. Taking into account an uncertainty in the determination of their t_0 of approximately 50 fs, which is based on how well the Coulomb channels can be fitted by the simulated Coulomb curves, the two data sets agree within the error bars.

As before, the internuclear distance is calculated from the mid-point of the step-function in the $(0, x)$ channel in panel (a) using Equation (8.22), and the corresponding internuclear distances for DFIB (black stars) and CH_3I (red squares) from this work are shown in Figure 8.27(b). Since the mean KER of the $(0, x)$ channel was experimentally determined to be between 0.37-0.38 eV from the kinetic energy distribution of I^{2+} and I^{3+} ions, this leads to an asymptotic total energy, E_{kin} , of 0.796 eV measured for the

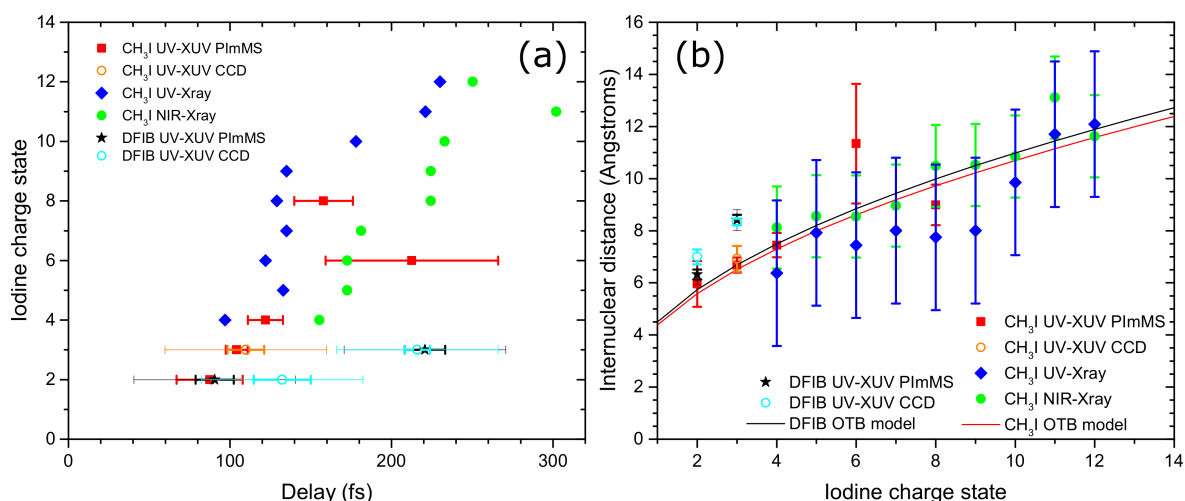


Figure 8.27: (a) Onset times of the low $(0, x)$ KER channel for various charge states of iodine following the UV photodissociation and subsequent XUV inner-shell ionization of DFIB (black star, this work), determined by the mean of a Gaussian cumulative distribution function fit. The corresponding values for CH₃I are also shown for UV-XUV (red square, this work), UV-Xray (blue diamond) [81] and NIR-Xray (green circle) [77]. The error bars used in this work correspond to the fitting error of the Gaussian CDF fit (thick error bars) and the fitting error of t_0 (thin error bars). The corresponding CCD data sets for DFIB (cyan circles) and CH₃I (orange circle) are also shown. (b) The internuclear distance in the onset of the $(0, x)$ KER channel corresponding to the delays in panel (a) are shown which were calculated using Equation (8.22). The critical distance calculated from the over-the-barrier classical model, using Equation (8.24), for DFIB (solid black line) and CH₃I (solid red line) are also shown.

neutral dissociation of DFIB in these measurements. An equilibrium separation, R_{eq} , of 491 pm was again used as determined by simulation of the Coulomb curves for the neutral dissociation of the molecule. The critical distance that charge transfer will cease to occur is predicted by the classical over-the-barrier (OTB) model (black line) using Equation (8.24) and an ionization energy of 9.6 eV for the 2,6-DFB radical [334]. In Figure 8.27(b), both I^{2+} and I^{3+} from DFIB appear above the OTB model line and may be explained by the influence of the electron-rich benzene ring, in which the delocalized electrons could make it easier for an electron to transfer onto the iodine fragment than in the case of CH₃I. Consequently, this could lead to a longer delay in the onset of the $(0, x)$ channel.

8.5 Conclusions

In conclusion, the photodissociation and charge transfer dynamics of CH₃I and DFIB were investigated with both a conventional CCD camera and a time-stamping device, the PImMS1 camera. Simulation of the Coulomb channels revealed that the UV pulse induced a neutral dissociation of the C-I bond in the parent molecule to generate two neutral fragments:



The XUV pulse then ionized the neutral fragments. If both fragments were charged after the UV and XUV pulses, then a Coulomb channel appeared in the delay-dependent kinetic energy maps of multiply charged iodine fragments. If one or both fragments were neutral after the after interaction with both pulses, then a $(0, x)$ channel appeared where the kinetic energy in the channel remained constant at all time delays.

In CH₃I, Coulomb channels appeared in the I³⁺, I⁴⁺, I⁵⁺, and I⁶⁺ fragments that were partnered with a singly charged co-fragment, CH₃⁺ in all cases. A delay in the onset of the $(0, x)$ channel was observed as a consequence of charge transfer. A higher charge state of iodine also lead to an increased delay in the onset of this $(0, x)$ channel since charge transfer was possible for longer delays (and therefore over larger distances) between CH₃ and the highly charged iodine, I^{x+}. It should also be noted that the spin-orbit channels of iodine were imaged using the CCD camera in the I³⁺ ion, with a Φ^* value of 0.61 observed in this work. Although the Coulomb channel in I³⁺ was relatively broad, there was an excellent agreement between the simulated curve for CH₃ + I* and the experimental Coulomb channel. The simulated CH₃ + I channel also had a good agreement with the experimental Coulomb channel.

In DFIB, a very intense DFB⁺ + I³⁺ Coulomb channel was accompanied by a weak DFB²⁺ + I³⁺ Coulomb channel in I³⁺. The I²⁺ ion had a weak DFB⁺ + I²⁺ Coulomb

channel that disappeared after ~ 200 fs, and coincided with the appearance of the $\text{DFB} + \text{I}^{3+}(0, x)$ channel. Both these channels disappeared and appeared with a delay which corresponded to charge transfer between $\text{DFB} + \text{I}^{3+}$ to $\text{DFB}^+ + \text{I}^{2+}$. Charge transfer in the I^{2+} ion was also observed through the delay in the onset of the $\text{DFB} + \text{I}^{2+}(0, x)$ channel. The delay in the onset of this $(0, x)$ channel, as mentioned earlier, is due to charge transfer. This $(0, x)$ channel will only appear at a pump-probe delay that is large enough, corresponding to a large distance between the fragments, for charge transfer to cease.

The delay in the onset of the $(0, x)$ channels were converted into internuclear distances, which agreed well with the classical over-the-barrier model and previous work by Erk *et al.* and Boll *et al.* on UV-Xray and NIR-Xray measurements on CH_3I , respectively [77, 81].

In the following chapter, a brief summary of the work presented in this thesis is given, and is accompanied by a discussion on future work.

Chapter 9

Conclusions and Future Work

In the 3D measurements presented in this thesis, the PImMS camera successfully captured the full three-dimensional velocity distribution of CO^+ and S^+ ions in the one-colour photodissociation of OCS at 230 nm. A new VMI design which couples the current DC slice imaging set-up with an additional electrostatic plate that is pulsed has been previously proposed in the method of post-extraction Newton-sphere inversion (PENI) [235, 335, 336]. In PENI [235, 335, 336], the Newton sphere of ions is inverted and stretched along the ToF coordinate by using an additional (fifth) electrostatic plate that is pulsed ‘on’ at a particular point in time called the switch time, t_s . Figure 9.1 shows the 3D potential energy view of the PENI setup [235, 335, 336] when the fifth electrode is kept grounded during the acquisition window, as in panel (a), and after the switch time when the plate pulsed is ‘on’ by applying a voltage, as in panel (b).

By pulsing this fifth electrode from ground to a very high voltage (~ 2000 V), the Newton sphere of ions suddenly appear on the falling slope of a potential energy hill [235, 336], and the back (slow) portion is accelerated more than the front (fast) portion. This leads to the inversion and subsequent stretching of the Newton sphere along the ToF coordinate [235, 336]. Simulations of this new VMI design using a genetic algorithm optimization approach have been carried out by Felix Allum and have shown that six times as many time-resolved slices can be recorded through the Newton sphere of ions as compared to a conventional DC slice imaging method, whilst maintaining

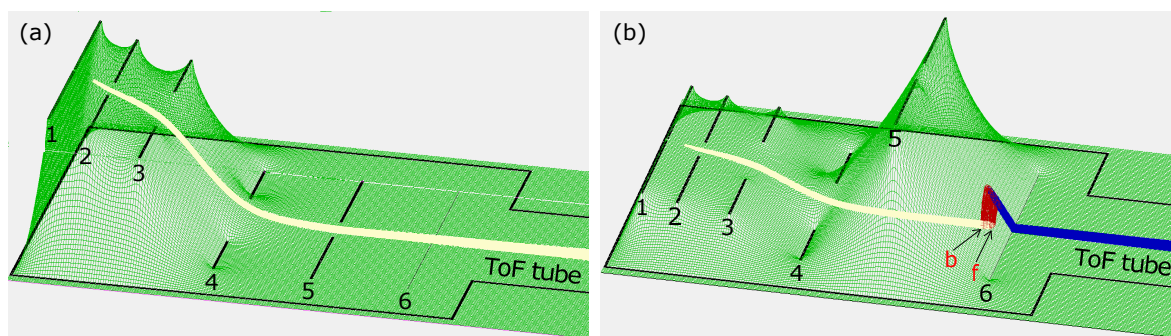


Figure 9.1: Three-dimensional potential energy view of the PENI setup that was simulated using the SIMION 8.1 ion trajectory simulation package [173]. The six electrostatic electrodes used in this design are: the repeller plate (1), the extractor plate (2), the third lens plate (3), a grounded plate (4), a pulsed plate (5), and a grounded mesh (6). A field-free region exists in the ToF tube which leads to the detector. Panels (a) and (b) correspond to the pulsed plate being kept grounded throughout the acquisition window or pulsed to a set voltage at the switch time, respectively. In the latter, a potential energy hill appears at the switch time. In panel (b), the ion trajectories before (white), during (red) and after (blue) the switch time are shown, and the forward (f) and backward (b) portion of the distribution of ions is also indicated.

good velocity-mapping conditions.

In the measurements of difluoriodobenzene (DFIB) and dihydroxybromobenzene (DHBB), the CEI technique coupled with the PImMS2 camera and covariance analysis was used to identify the four isomers of DFIB and two isomers of DHBB. In a mixture measurement, it was determined that 3,5-DFIB and 2,4-DFIB were present in a 2:1 ratio. In the case of DHBB, strong correlations were observed with OH^+ and other ions, which provided significant structural information on the 2,5-DHBB and 2,6-DHBB isomers. These findings open up opportunities to study biologically relevant molecules such as carbohydrates and amino acids [292], which contain hydroxy ($-\text{OH}$) and amine ($-\text{NH}_2$) substituent groups.

The CEI technique and covariance analysis was extended to the time-resolved study of *trans-cis* isomerization of 4,4'-difluoroazobenzene. Although time-dependent features were observed in the raw and background subtracted recoil-frame covariance maps, the presence of either or both *cis*-DFAB and vibrationally hot *trans*-DFAB could not be confirmed. The accuracy of the background subtraction (*i.e.* ground state *trans*-DFAB) method is particularly crucial in these types of measurements. Future experiments could implement a shot-to-shot background subtraction approach where

background signal is recorded on alternate shots. The type of substituent groups in the molecule is particularly important in order to observe meaningful angular correlations between recoil ions following the Coulomb explosion of the molecule. Possible future work on time-resolved *trans-cis* isomerization reactions could be attempted on *trans*- and *cis*-stilbene, which are commercially available and do not isomerize in a heated nozzle.

The FEL-related measurements successfully demonstrated the Coulomb explosion of molecules through inner-shell ionization. The FEL provided access to the multi-photon inner-shell ionization regime which generated highly charged recoil fragments. In the case of iodine, charge states of +8 and +3 were observed in CH_3I and 2,6-DFIB, respectively, at the FEL intensities used. The charge transfer dynamics between the multiply charged iodine and co-fragment were imaged using the PImMS1 camera. The one-photon neutral dissociation of those molecules was also imaged with the PImMS1 camera to track the kinetic energies of multiply charged iodine fragments over the course of the dissociation. Simulations of the resulting Coulomb features in the delay-dependent kinetic energy maps confirmed that the UV pulse generated neutral iodine with a neutral co-fragment.

The PImMS2 camera was used in a second, separate FLASH beamtime, the results of which were not discussed in this thesis. In these measurements, CH_2ICl was investigated to gain an insight into the influence of a second halide in the charge transfer and photodissociation dynamics of the molecule. Several differences are present in UV-XUV, IR-XUV and UV-IR pump-probe measurements that have been extensively analysed, and will be discussed in a forthcoming publication. In the same beamtime, time-dependent effects were observed in the electron data that are not observed in the ion data. In the electron data, analyzed by Felix Brausse and Gildas Goldztein, a shift in the kinetic energy of the iodine 4d electron is observed which gives an insight into how (and how fast) the electronic structure changes upon dissociation. Future FEL experiments could be carried out on larger, biologically relevant molecules such as peptides using an electrospray source [337]. Meaningful angular covariances between recoil ions could not be extracted from the ion data in this second beamtime, even though

the detector were operated at optimum settings. This is most likely due to the instability of the FEL. A more advanced version of the covariance method, called partial covariance, has been previously used by Frasinski *et al.* [309] to correct for shot-to-shot fluctuations in the FEL.

TimePix3, which is a next generation pixel-based time-stamping device, could be used in 3D imaging and CEI covariance imaging experiments. Using its 1.56 ns time-precision, it unlocks the possibility of recording the full Newton sphere of ions with up to eight times more slice images than those shown with the PImMS camera in this thesis, which amounts to approximately 100 time-slices. TimePix3 coupled with the method of PENI could potentially record hundreds (up to 600) of time-resolved slices through the Newton sphere. The 1.56 ns time-precision could also be used to investigate the three-dimensional angular covariance of recoil ions using three-dimensional two- and three-fold covariance imaging to obtain three-dimensional structural information on the molecule.

Developments of the PImMS technology include the use of microlenses and single-photon avalanche detectors (SPAD) arrays. In the former, a tiny micron-sized lens is placed on top of each PImMS pixel to focus the incident light onto the four diodes which make up the overall active array of the pixel, thus significantly improving the sensitivity of the PImMS sensor. First results with a microlens set-up that is installed on a PImMS2 sensor (μ PImMS2) show that the sensitivity of the PImMS2 sensor has been significantly improved. Experiments in the near future are planned to quantify the improvement in sensitivity of PImMS sensors that use microlenses.

SPAD arrays provide the opportunity of detecting low-intensity signals down to single photons. Particles impacting on the detector generate an electron-ion pair through impact ionization, which subsequently triggers an avalanche current [338, 339] that, in turn, triggers a signal. Not only do these detectors provide high-sensitivity but they also offer the opportunity to reduce the timing precision well below 1 ns since the timing jitter in SPAD arrays is on the order of only a few tens of picoseconds [339–341].

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Appendix A

Recoil-Frame Covariance Maps

A.1 DFIB/DHBB Isomers

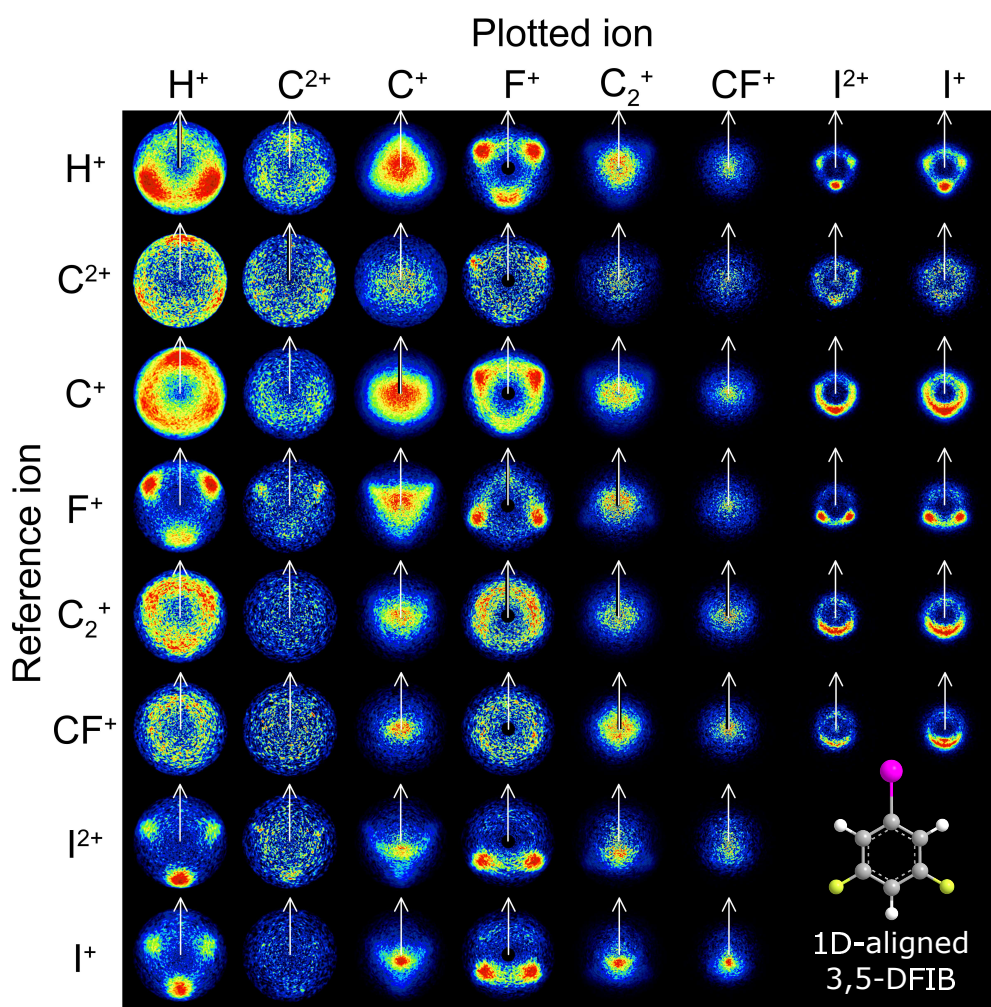


Figure A.1: Experimental two-fold covariance maps for 1D-aligned 3,5-DFIB molecules following strong-field ionization with an intense 800 nm pulse recorded with the PImMS2 camera. The reference and plotted ions that each map can be identified by the assignments given by the respective row and column. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map.

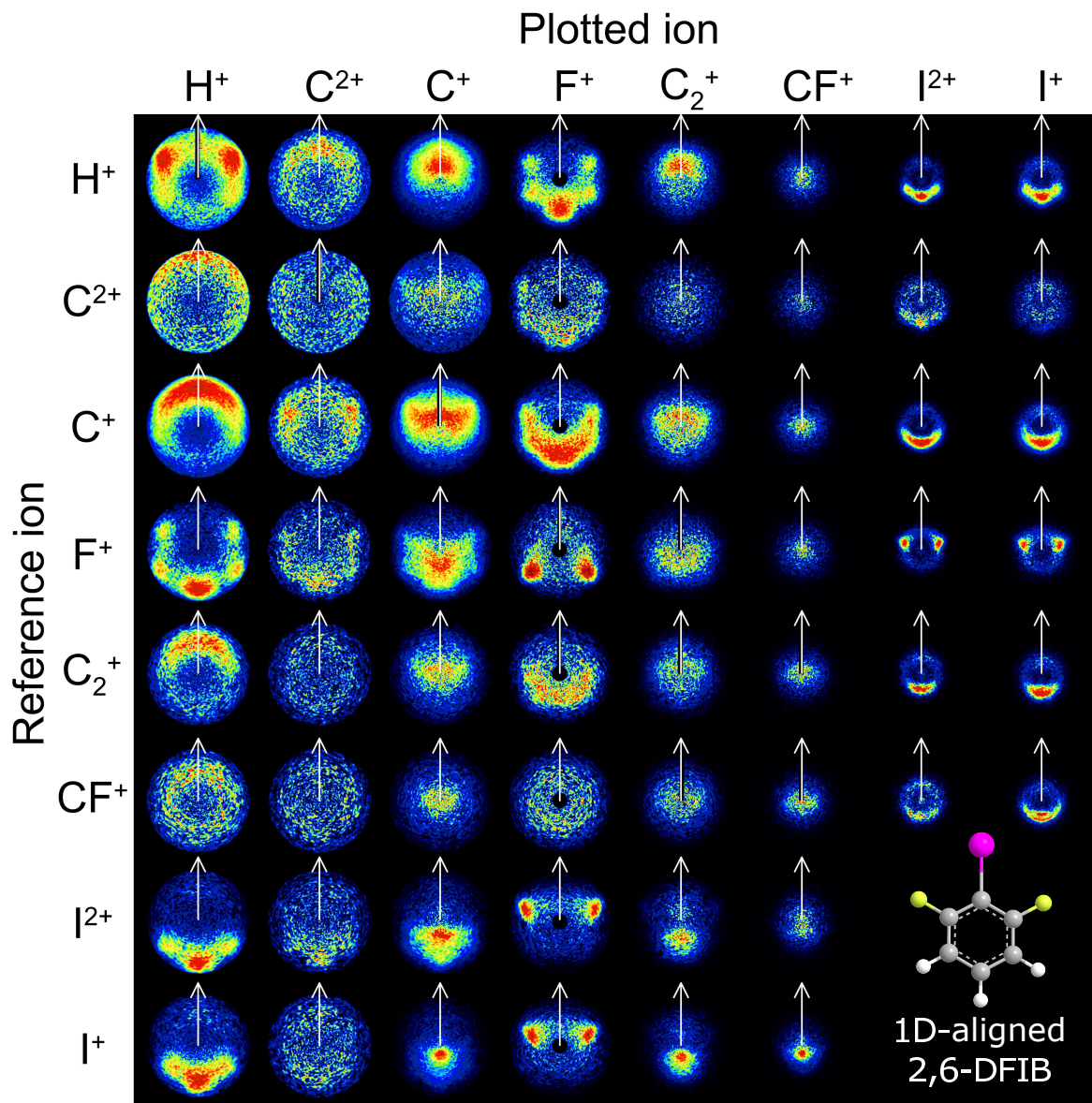


Figure A.2: Similar to Figure A.1, showing experimental two-fold covariance maps for 1D-aligned 2,6-DFIB molecules following strong-field ionization with an intense 800 nm pulse recorded with the PImMS2 camera. The reference and plotted ions that each map corresponds to can be identified by the assignments given by the respective row and column. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map.

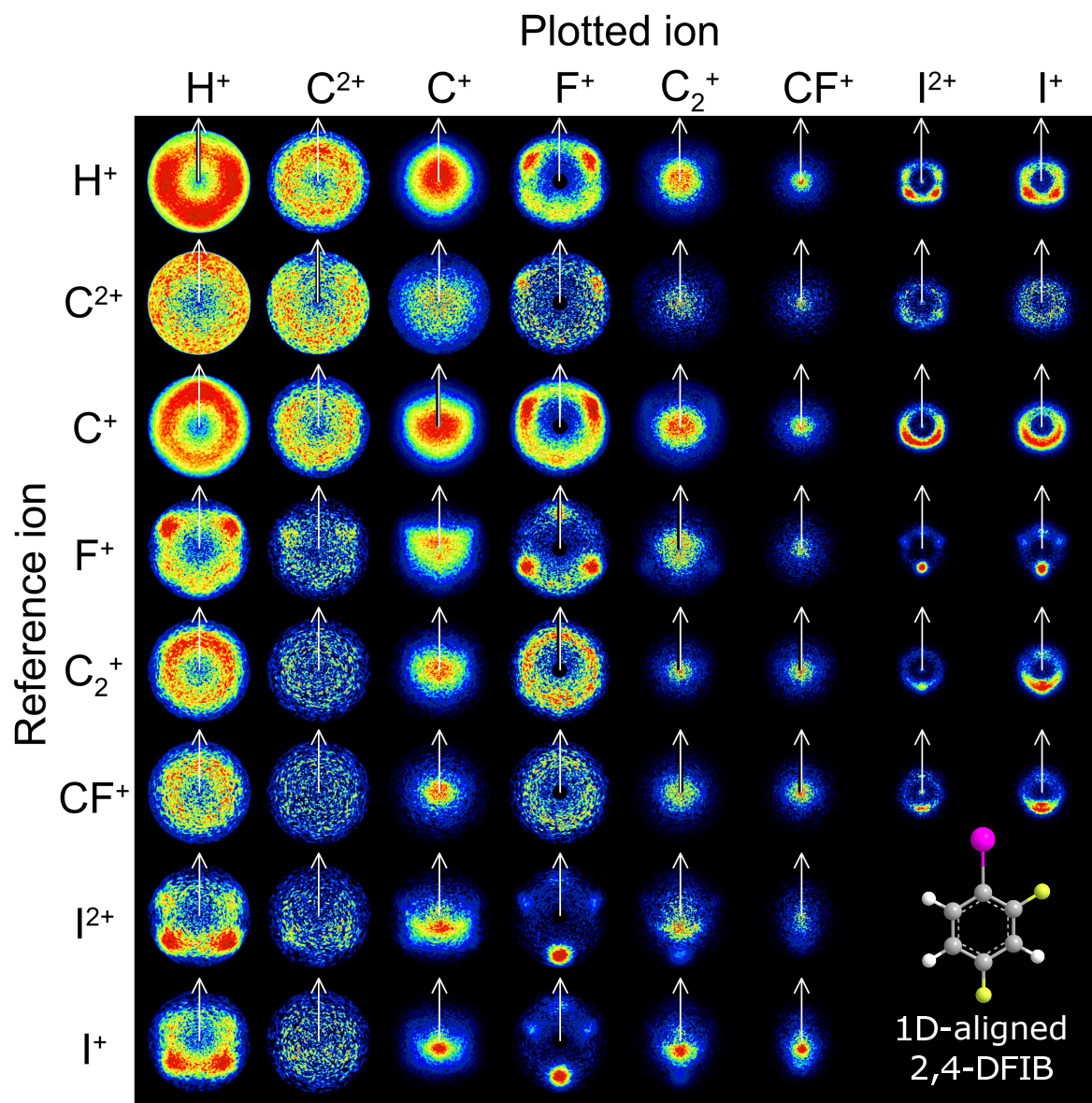


Figure A.3: Similar to Figure A.1, showing experimental two-fold covariance maps for 1D-aligned 2,4-DFIB molecules following strong-field ionization with an intense 800 nm pulse recorded with the PImMS2 camera. The reference and plotted ions that each map can be identified by the assignments given by the respective row and column. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map.

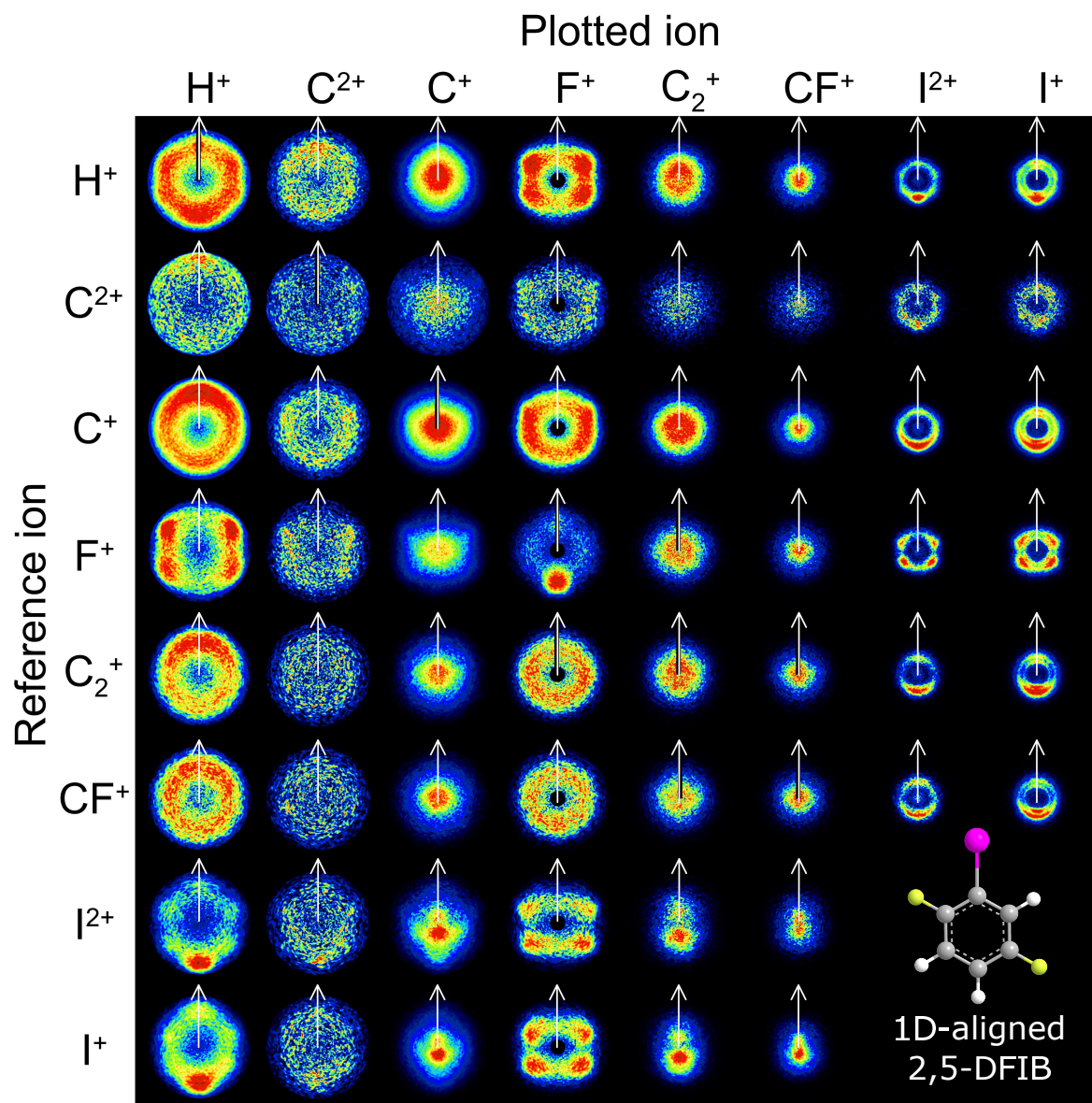


Figure A.4: Similar to Figure A.1, showing experimental two-fold covariance maps for 1D-aligned 2,5-DFIB molecules following strong-field ionization with an intense 800 nm pulse recorded with the PImMS2 camera. The reference and plotted ions that each map can be identified by the assignments given by the respective row and column. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map.

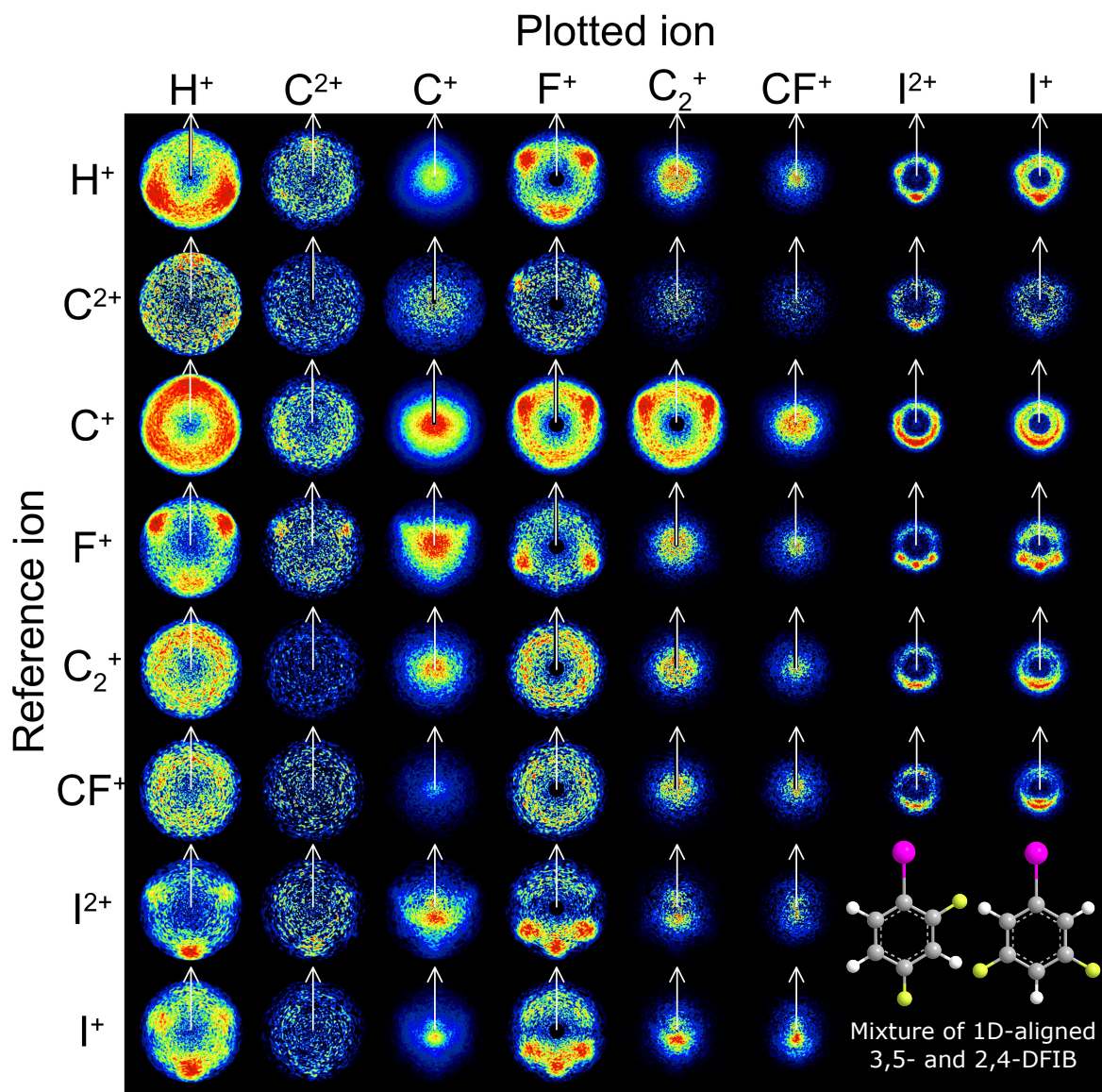


Figure A.5: Similar to Figure A.1, but showing experimental two-fold covariance maps for a mixture of 1D-aligned 3,5- and 2,4-DFIB molecules following strong-field ionization with an intense 800 nm pulse recorded with the PImMS2 camera. The reference and plotted ions that each map corresponds to can be identified by the assignments given by the respective row and column. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map.

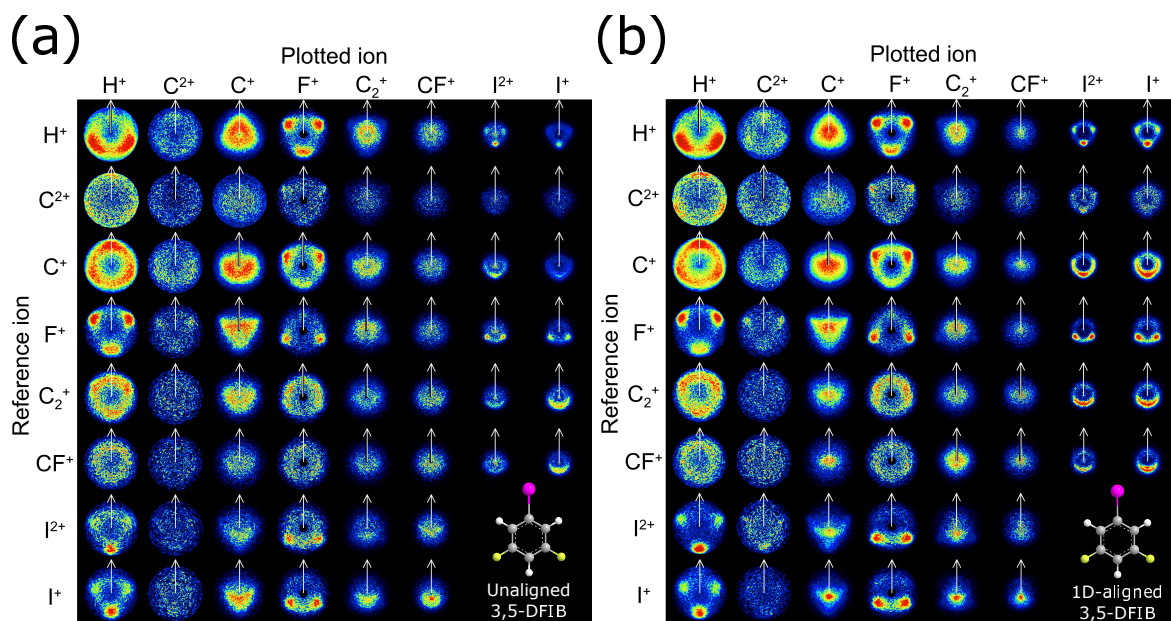


Figure A.6: Experimental two-fold covariance maps are presented for (a) Unaligned and (b) 1D-aligned 3,5-DFIB molecules following strong-field ionization with an intense 800 nm pulse recorded with the PImMS2 camera. The 1D-aligned maps are identical to those in Figure A.1. The reference and plotted ions that each map corresponds to can be identified by the assignments given by the respective row and column. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map.

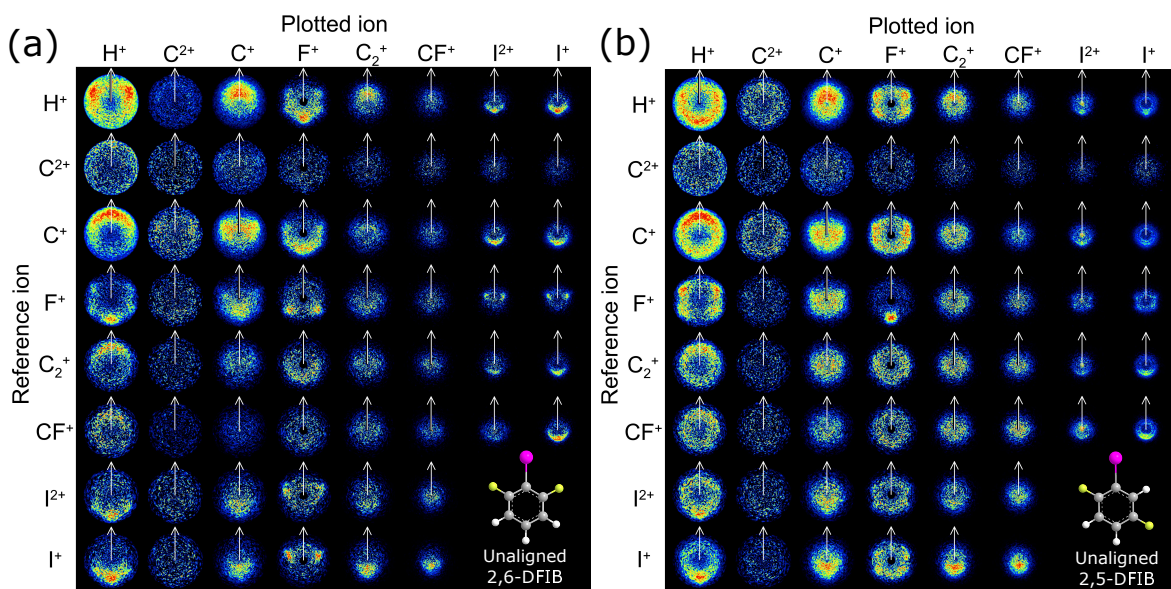


Figure A.7: Experimental two-fold covariance maps for unaligned (a) 2,6-DFIB and (b) 2,5-DFIB molecules following strong-field ionization with an intense 800 nm pulse recorded with the PImMS2 camera. The reference and plotted ions that each map corresponds to can be identified by the assignments given by the respective row and column. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map.

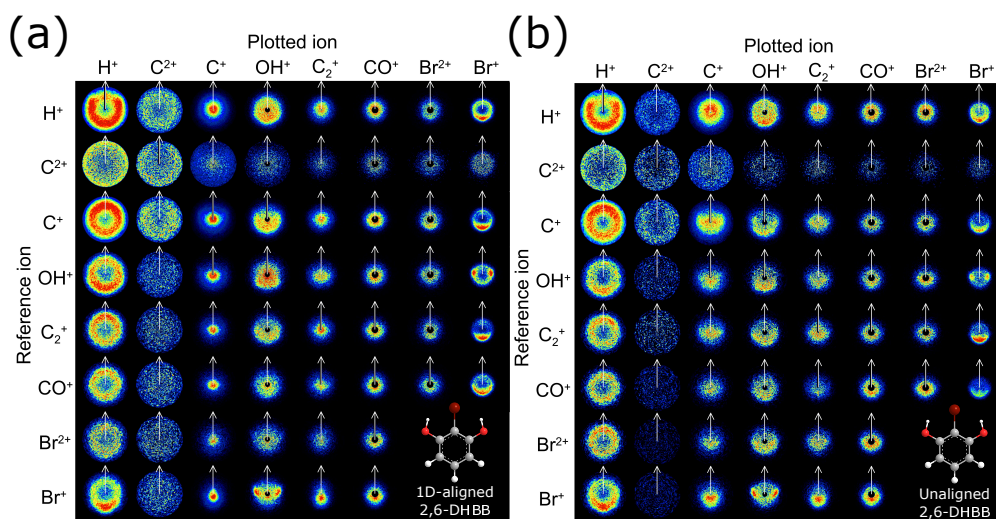


Figure A.8: Experimental two-fold covariance maps are presented for (a) 1D-aligned and (b) unaligned 2,6-DHBB molecules following strong-field ionization with an intense 800 nm pulse recorded with the PImMS2 camera. The reference and plotted ions that each map corresponds to can be identified by the assignments given by the respective row and column that the image is taken from, respectively. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map.

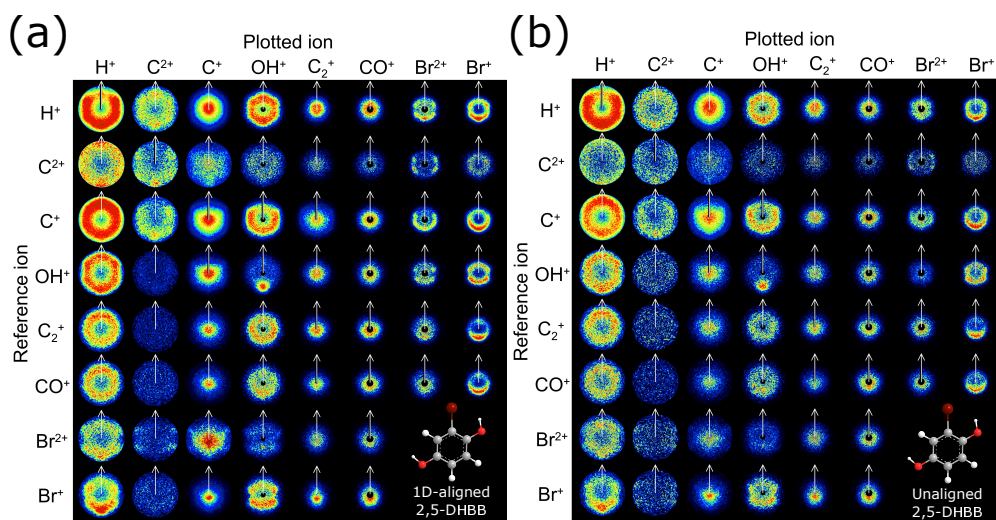


Figure A.9: Similar to Figure A.8, but showing experimental two-fold covariance maps for (a) 1D-aligned and (b) unaligned 2,5-DHBB molecules following strong-field ionization with an intense 800 nm pulse recorded with the PImMS2 camera. The reference and plotted ions that each map corresponds to can be identified by the assignments given by the respective row and column that the image is taken from, respectively. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map.

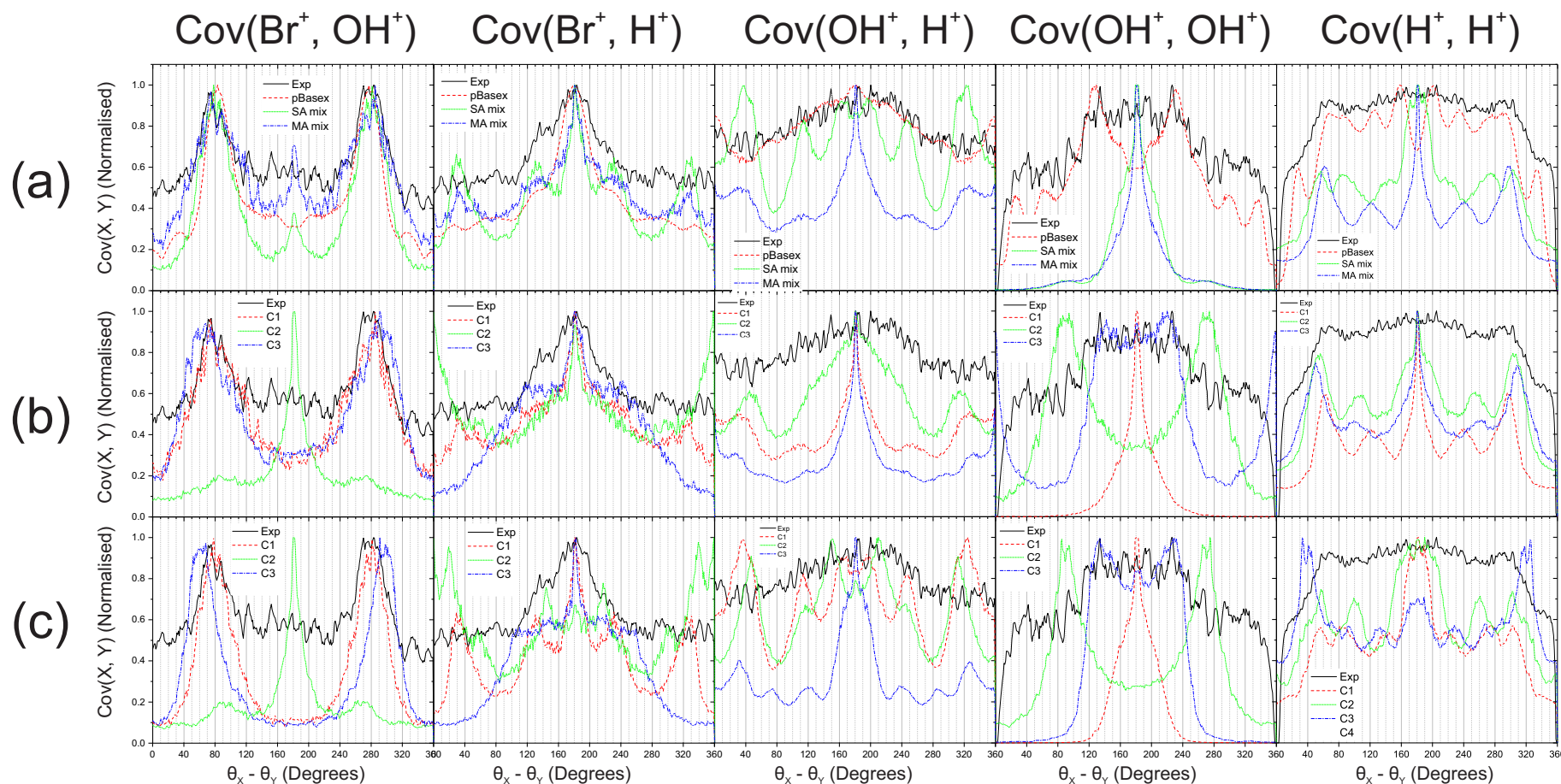


Figure A.10: Angular distributions of two-fold covariance maps of 1D-aligned 2,6-DHBB molecules shown in Figure 5.20. (a) Simulated results for the three conformers (coloured traces) of 2,6-DHBB using the single atom model are shown alongside the experimental distribution (black solid trace). (b) Similar to panel (a) but showing simulated results from the multi atom model. (c) The simulated data for a mixture containing conformers 1 and 2 in a 88:12 ratio are shown from the single atom (green dotted trace) and multi atom (blue dashed dotted trace) models alongside the experimental data (black solid trace) and the corresponding pBasex data (red dashed trace). All distributions have been normalised to their corresponding maximum intensity.

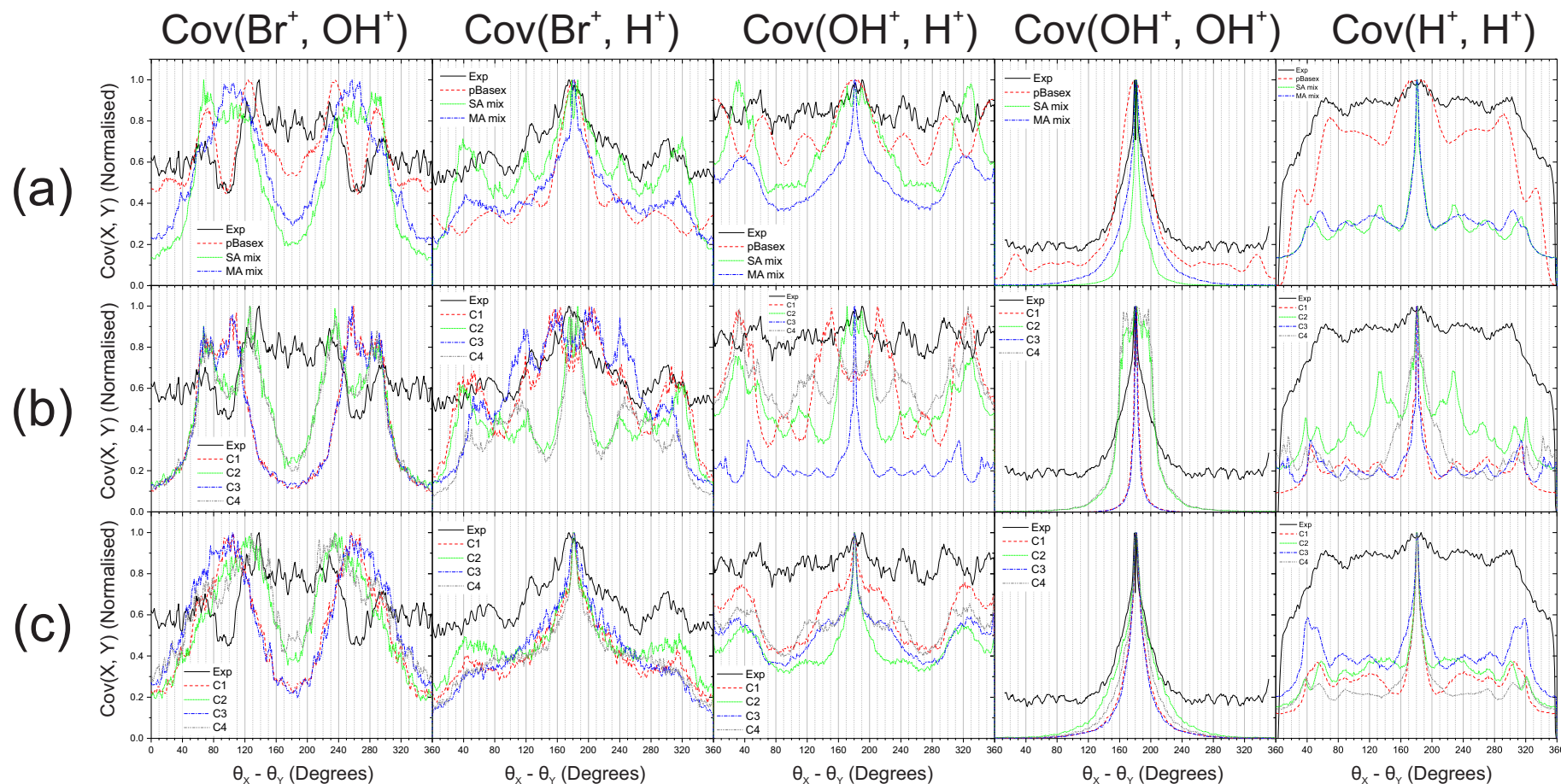


Figure A.11: Similar to Figure A.10 but for two-fold covariance maps of 1D-aligned 2,5-DHBB molecules shown in Figure 5.21. (a) Simulated results for the four conformers (coloured traces) of 2,6-DHBB using the single atom model are shown alongside the experimental distribution (black solid trace). (b) Similar to panel (a) but showing simulated results from the multi atom model. (c) The simulated data for a mixture containing conformers 1 and 2 in a 1:1 ratio are shown from the single atom (green dotted trace) and multi atom (blue dashed dotted trace) models alongside the experimental data (black solid trace) and the corresponding pBasex data (red dashed trace). All distributions have been normalised to their corresponding maximum intensity.

A.2 *Trans-Cis* Isomerization of DFAB

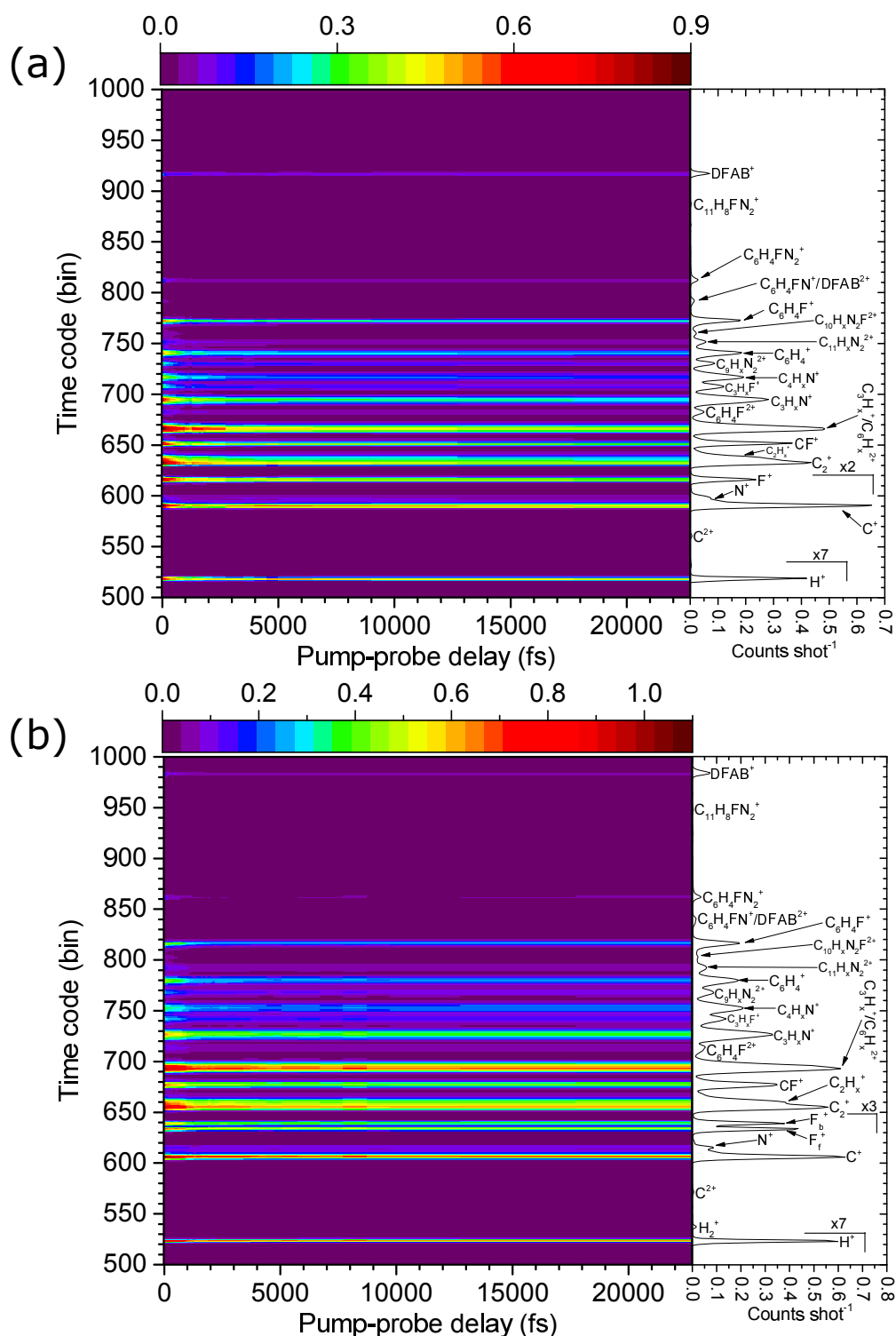


Figure A.12: Maps of time-of-flight spectra as a function of pump-probe delay are shown for 4,4'-difluoroazobenzene (DFAB) molecules following photoexcitation by a 330 nm pulse and strong-field ionization with an intense 800 nm pulse. Both pulses were polarized either (a) parallel or (b) perpendicular to the detector plane. The inset on the right hand of both panels shows the annotated probe-only ToF spectra. Each ToF distribution was normalised to its corresponding total number of laser shots.

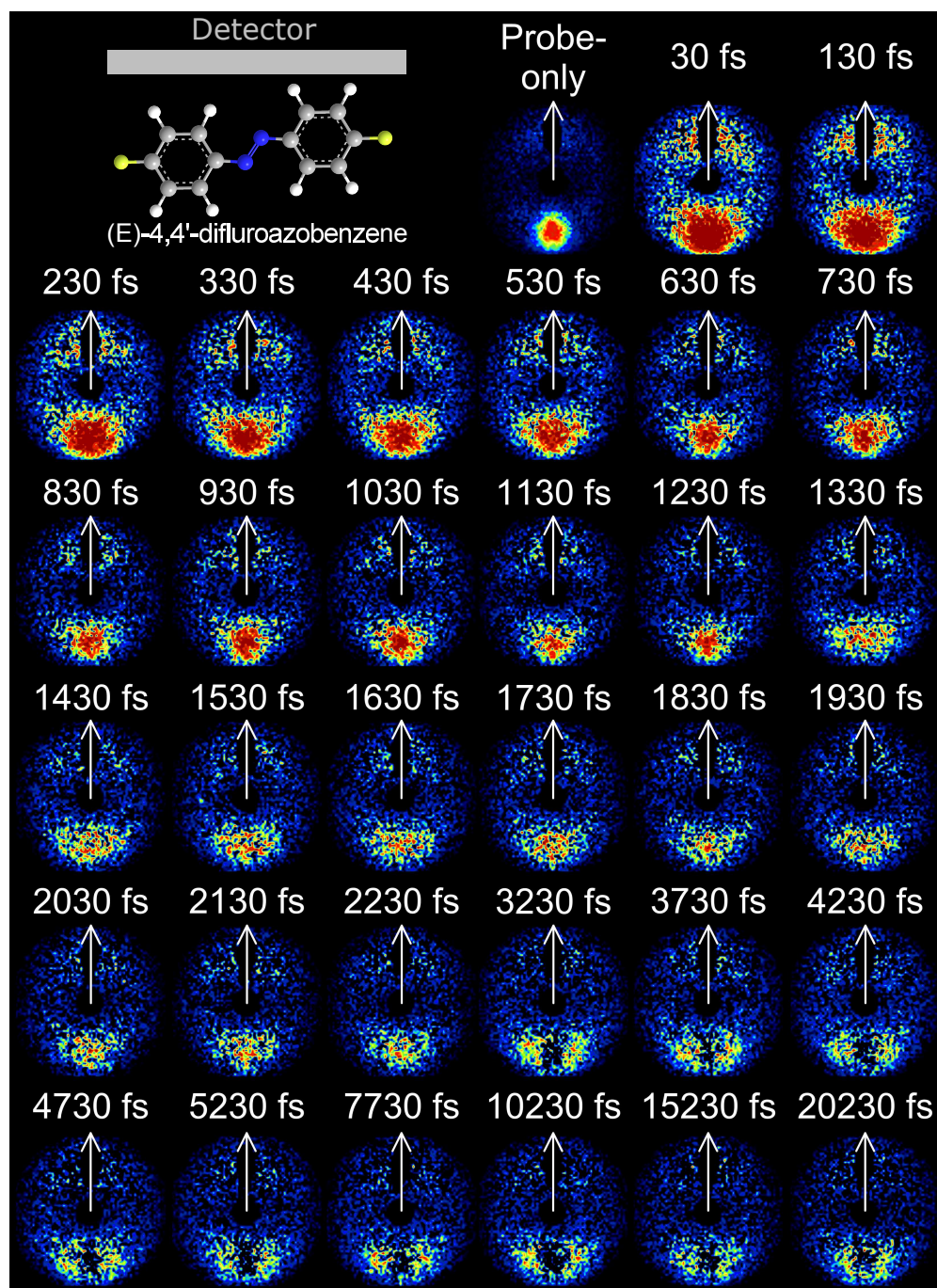


Figure A.13: The probe-only subtracted experimental two-fold covariance maps, $\text{Cov}(\text{F}^+, \text{F}^+)$, in the parallel configuration are presented for unaligned 4,4'-difluoroazobenzene molecules following UV-pump and strong-field ionization by 330 nm and 800 nm pulses which were recorded by the PImMS1 camera. Here, one of the fluorines is chosen as the reference ion and the other is shown as the plotted ion in each map. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map. The labels above each map indicate the probe-only and the corresponding pump-probe delay that each map corresponds to. The raw probe-only map is shown. During the subtraction process, the probe-only data was scaled down by a factor of 0.65 to generated to corresponding pump-probe subtracted data.

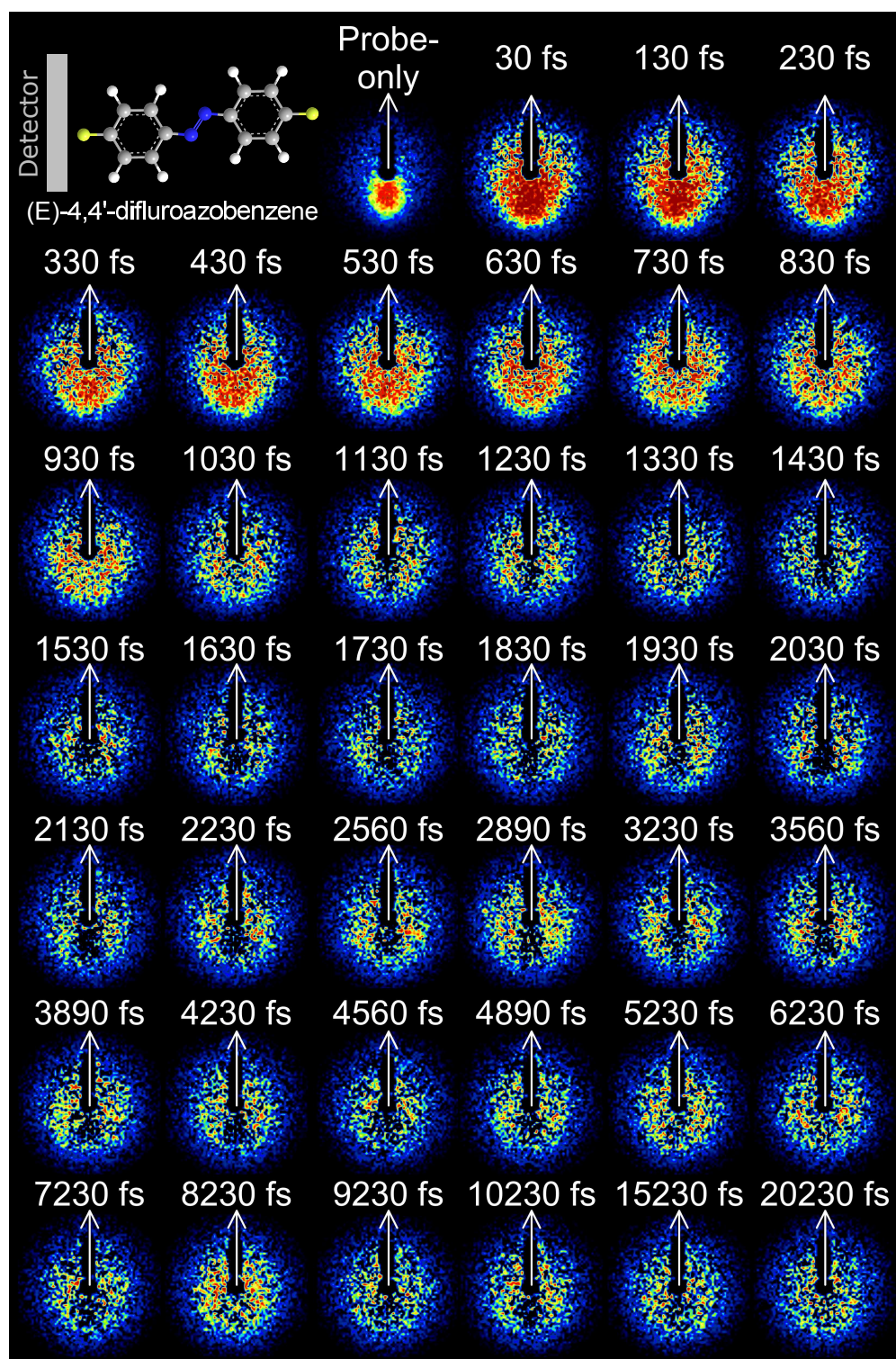


Figure A.14: Similar to Figure A.13 but for the perpendicular configuration. Here, one of the fluorines is chosen as the reference ion and the other is shown as the plotted ion in each map. The reference ion is confined to a vertical vector from the centre of the covariance map to the top edge, as indicated by the white arrow in each map. The labels above each map indicate the probe-only and the corresponding pump-probe delay that each map corresponds to. The raw probe-only map is shown. During the subtraction process, the probe-only data was scaled down by a factor of 0.65 to generated to corresponding pump-probe subtracted data.