

## Chapter 2

# Experimental Techniques and Methods of Data Analysis

This chapter details the experimental methods and apparatus used in the work presented in this thesis. The experiments were performed in two separate laboratories: that of Prof. Mark Brouard at the University of Oxford, and that of Prof. Henrik Stapelfeldt at the University of Aarhus. Both apparatus are variants of a conventional velocity-map ion imaging (VMI) spectrometer. The fundamental principals of velocity-map ion imaging were introduced in Sect. 1.5 and are reviewed briefly here, whereafter each spectrometer is described in detail. The Pixel Imaging Mass Spectrometry (PImMS) camera, which is central to the work undertaken in this thesis, is introduced and the design and function of the device are described in detail. Experimental results are presented characterising the performance and characteristics of the device. In addition to experimental methods, this chapter also describes the various data analysis routines used to extract scientifically pertinent information from the experimental data.

### 2.1 Experimental Principles

The data presented in this thesis were collected using variants of a conventional velocity-map ion imaging experiment, as illustrated in Fig. 1.4. Although such apparatus differ in their details, the general construction is similar in each case. The apparatus generally consist of a series of chambers kept under high ( $<10^{-5}$  Torr) or ultra-high ( $<10^{-8}$  Torr) vacuum conditions, typically through the use of turbomolecular and/or diffusion pumps. The sample gas is supersonically expanded into the experiment through a pulsed valve and subsequently passes through one or more skimmers to produce a collimated and rotationally cold (typically  $<25$  K) molecular beam. The molecular beam is then intersected by one or more focussed laser pulses to induce a structural or chemical change in the target molecules, and to

cause photoionisation of the resultant photofragments. The nascent ions are then accelerated and focussed down a flight tube onto a two-dimensional detector by an electric field, tuned such that velocity-mapping of the ions takes place, as discussed in Sect. 1.5.1. A further consequence of the use of an electric field to extract the ions onto the detector is that the ions are separated temporally at the detector according to their mass-to-charge ( $m/z$ ) ratio. The detector consists of a set of microchannel plates (MCPs) and a phosphor screen. The impact of the ions onto the detector causes flashes of light to be emitted by the phosphor screen, which are imaged by a camera.

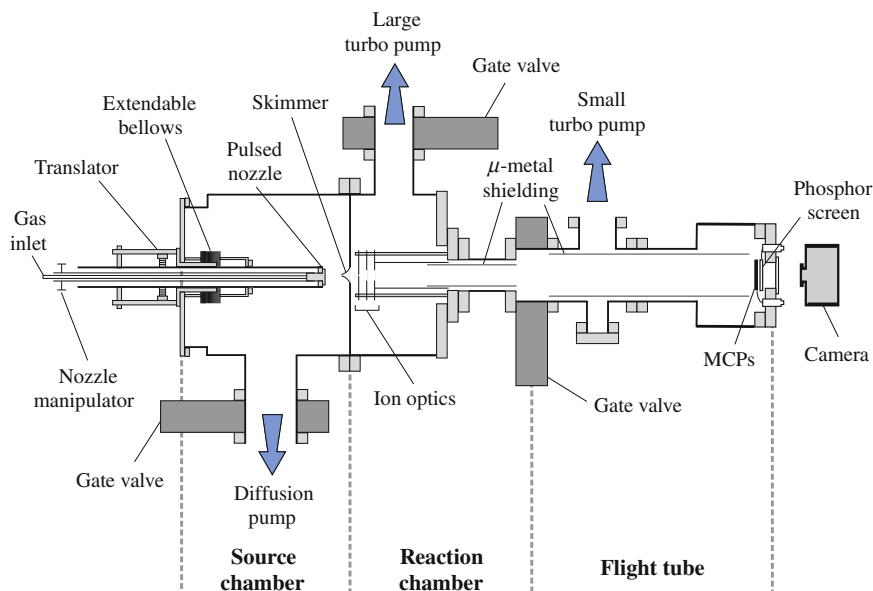
## 2.2 The Oxford VMI Spectrometer

The Oxford spectrometer was used for the PImMS characterisation experiments (Sect. 2.5.4), the three-dimensional imaging experiments (Chap. 3), and the proof-of-principle electron-ion pulsed extraction experiments (Chap. 4). The experiment is located in the laboratory of Prof. Mark Brouard in the Chemistry Research Laboratory at the University of Oxford.

### 2.2.1 Overview

The experiment comprises three main vacuum chambers: the source chamber, the reaction chamber, and the flight tube. A schematic of the experiment is shown in Fig. 2.1. The sample gas is introduced to the source chamber by way of a supersonic expansion through a pulsed (10 Hz) General Valve (Series 9) at a backing pressure of approximately 0.5–2 bar, supplied from an external stainless steel sample reservoir fitted with a two-stage regulator. The General valve is mounted in such a way that it is possible to translate the valve orifice fully in three-dimensional space relative to the fixed position of the skimmer, allowing for optimisation of the experimental signal. The rotational temperature of the molecular beam has been measured previously to be approximately 25 K [1]. The source chamber is pumped by a  $3700\text{ l s}^{-1}$  water-cooled diffusion pump (Varian VHS-250), backed by a rotary pump (Leybold Trivac D40V). The diffusion pump is fitted with a water-cooled baffle located between the pump and the chamber in order to minimise contamination of the apparatus by the diffusion pump oil vapour. Background pressures in the source chamber are typically around  $1 \times 10^{-6}$  Torr, rising to approximately  $2 \times 10^{-5}$  Torr when the molecular beam is in operation.

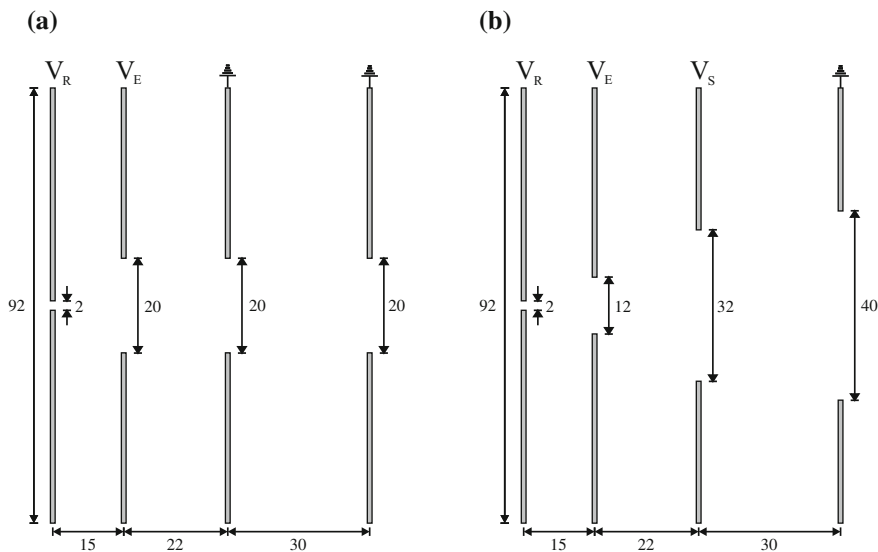
The source chamber is separated from the reaction chamber by a skimmer with an orifice of 1 mm diameter (BeamDynamics Inc.), through which the supersonic expansion passes in order to produce a collimated molecular beam. The reaction chamber contains the ion optics assembly (see Sect. 2.2.2) and is differentially pumped by a  $510\text{ l s}^{-1}$  turbomolecular pump (Pfeiffer, Vacuum TMH-521P), backed by a rotary pump (Leybold, Trivac D40V), to a typical background pressure of around



**Fig. 2.1** Schematic illustration of the Oxford velocity-map ion imaging spectrometer

$2 \times 10^{-7}$  Torr. The laser beams enter through fused silica windows on either side of the reaction chamber to intersect the molecular beam in a perpendicular geometry between the repeller and extractor electrodes of the ion optics assembly. The windows are fitted internally with home-built light baffles to minimise the amount of scattered light entering the chamber. Each of the baffles consists of a stack of copper rings contained within a stainless steel housing. The surfaces of the copper rings were oxidised in an alkaline solution of potassium persulphate [2] to increase their absorbance in the visible and UV wavelength range, and to diffuse the small amount of reflected light.

The flight tube is separated from the reaction chamber by a gate valve and is pumped by a small turbomolecular pump with a capacity of  $60 \text{ l s}^{-1}$  (Pfeiffer, Vacuum TMU 071P) backed by the same Leybold Trivac D40V rotary pump as the reaction chamber turbomolecular pump. The background pressure of the flight tube is of a similar order to that in the reaction chamber. The gate valve allows the reaction and source chambers to be vented while maintaining a vacuum in the flight tube, thereby protecting the detector from exposure to atmospheric gases. The flight tube is shielded along its length by a double-layered, cylindrical  $\mu$ -metal magnetic shield in order to neutralise the effect of stray magnetic fields on the trajectories of the ions and electrons in the field-free drift region.



**Fig. 2.2** Schematic representation of the two variants of ion optics arrangements used in the Oxford spectrometer. The ion optics consist of four disc shaped electrodes, each with a central aperture. The electrodes are referred to as (from *left*) the repeller, extractor, slice, and ground electrodes. The values  $V_R$ ,  $V_E$ , and  $V_S$  refer to the voltages applied to the repeller, extractor, and slice electrodes, respectively. All measurements are in mm. **a** Crush velocity map imaging. **b** dc slice velocity map imaging

### 2.2.2 Ion Optics

The ion optics assembly is mounted on the main flange of the reaction chamber by four threaded stainless steel rods, as illustrated in Fig. 2.1. The ion optics consist of a stack of circular stainless steel plates of thickness 1 mm, each possessing a central aperture of a carefully selected diameter, through which the ions are accelerated. The ion optics are separated from one another and insulated from the stainless steel mounting rods by MACOR<sup>®</sup> spacers. Depending on whether crush or dc slice imaging is to be effected (see Chap. 3), one of two alternative ion optics arrangements may be used (see Fig. 2.2). The final electrode was held at ground in each case in order to shield the flight tube from the potentials applied to the focussing lenses.

The electrostatic lenses were supplied with high voltages through three independent high-voltage MOSFET switches (Behlke, HTS 121, 12 kV, 30 A) so that the magnitude and polarity of the voltages may be switched on a short timescale ( $\sim 40$  ns). In order to reduce the capacitance of the system, and therefore the rise-time upon switching, the unit containing the Behlke switches is attached directly to the high voltage feedthroughs (SHV-10), which are mounted on a DN40 conflat (CF) flange fitted to the external wall of the reaction chamber.

### 2.2.3 Detector

The detection assembly consists of a pair of 78 mm chevron-stacked MCPs coupled to a P47 phosphor screen (Burle Technologies Inc.). The MCPs have a pore diameter of  $25\text{ }\mu\text{m}$  and a pitch of  $32\text{ }\mu\text{m}$ , giving a theoretical open area ratio of 55.4 %. The MCPs are fitted with a fine nickel mesh (Precision Eforming, MN4) with a pitch of 1.27 mm and a transmittance of 95 %. The mesh covers the front face of the MCPs and is located approximately 2 mm from the surface of the detector. The nickel mesh allows voltages to be applied to the front face of the detector while maintaining a field-free drift region in the flight tube. A photomultiplier tube fitted with a liquid light guide is used to measure the signal from the phosphor screen and provide a time-of-flight trace on an oscilloscope. Events on the phosphor screen are recorded by either an intensified CCD camera (Photonic Science,  $576 \times 768$  pixels) or the PImMS camera, which is described in detail in Sect. 2.5. The intensifier in the CCD camera is time-gated to allow the acquisition of images corresponding to individual peaks in the time-of-flight spectrum.

The high voltages required for operation are supplied through individual transformer units, which allows an additional pulse of up to 300 V to be independently applied to each face of the MCPs and the scintillator screen at independently determined times after the Q-switch trigger of the Nd:YAG laser. This allows for pulsing of the detector, to achieve a stepped gain profile during the course of each acquisition cycle. By altering the gain of the MCPs between the arrival times of the photoelectrons and photoions it is possible to optimise the detection efficiencies of each species. Since the gain profile of an MCP detector depends on the mass, kinetic energy, and chemical identity of the charged particle being detected [3], this is crucial to the success of the single detector photoelectron-photoion correlation experiments proposed in Chap. 4.

### 2.2.4 Optical Systems

The experiments performed using the Oxford VMI spectrometer were all of a single colour, that is that the pump and probe processes are at the same wavelength; therefore a single laser system was required in each case. The 446.41 nm radiation used for the experiments involving the photodissociation of molecular bromine was produced by a dye laser system (Lambda Physik, LPD 3000) pumped by the third harmonic (355 nm) of an Nd:YAG laser (Continuum, Powerlite Precision II) operating at 10 Hz. The third harmonic pulse energy of the Nd:YAG laser was approximately 420 mJ at full power, although this was attenuated to the desired level by increasing the time delay between the flashlamps and the Q-switch. The dye solution used was Coumarin 450 (also known as Coumarin 2) dissolved in ethanol, at a concentration of  $0.2\text{ g l}^{-1}$  in the oscillator and one third of that in the amplifier, producing a peak power output of  $\sim 10\text{ mJ}$  per pulse. The output of the dye laser was steered to the experiment using optical prisms and focussed into the reaction chamber by a 30 cm focal length lens.

For the experiments involving the photodissociation of ethyl iodide at around 245 nm the laser radiation was again provided by a dye laser system (Sirah, Cobra Stretch) pumped by the third harmonic of an Nd:YAG laser (Continuum, Powerlite Precision II). The maximum pulse energy of the third harmonic output was approximately 300 mJ, which was again attenuated by altering the delay between the flashlamps and the Q-switch of the laser. The dye solution used was Coumarin 503 (also known as Coumarin 307) dissolved in ethanol, at a concentration of  $0.2 \text{ g l}^{-1}$  in the oscillator and one fifth of that in the amplifier, giving a peak power output of  $\sim 23 \text{ mJ}$  per pulse at the fundamental wavelength. The frequency doubled output was produced using a BBO type I crystal (SHG 220) and was separated from the fundamental by a set of four Pellin-Broca prisms. The beam was then steered to the experiment using optical prisms and focussed into the reaction chamber using a 30 cm focal length lens.

### **2.2.5 Reagent Sources**

Both bromine and ethyl iodide are liquid at room temperature and pressure, and were prepared in the gas phase following the procedures outlined below. Both reagents have a tendency to form clusters in the gas phase unless the pressures and concentrations are kept sufficiently low.

#### **2.2.5.1 Bromine**

Liquid bromine was supplied from Fisher Scientific at a purity of 99 % and was decanted in small quantities into a sealed glass flask. The bromine was expanded into the stainless steel sample reservoir until it reached its vapour pressure. The bromine vapour was then successively diluted with helium to the appropriate concentration ( $< 1 \%$ ). Backing pressures of approximately 2 bar were used to supply the General Valve.

#### **2.2.5.2 Ethyl Iodide**

Ethyl iodide was supplied from Sigma-Aldrich at a purity of 99 % and was decanted in small quantities into a stainless steel 'cold finger'. The cold finger was cooled with liquid nitrogen and the residual atmospheric gases pumped off. The ethyl iodide was then allowed to warm to room temperature and expanded into the stainless steel sample reservoir until it reached its vapour pressure. The ethyl iodide vapour was then successively diluted with helium until the appropriate concentration was reached (approximately 5 %). Backing pressures of approximately 0.8 bar were used to supply the General Valve.

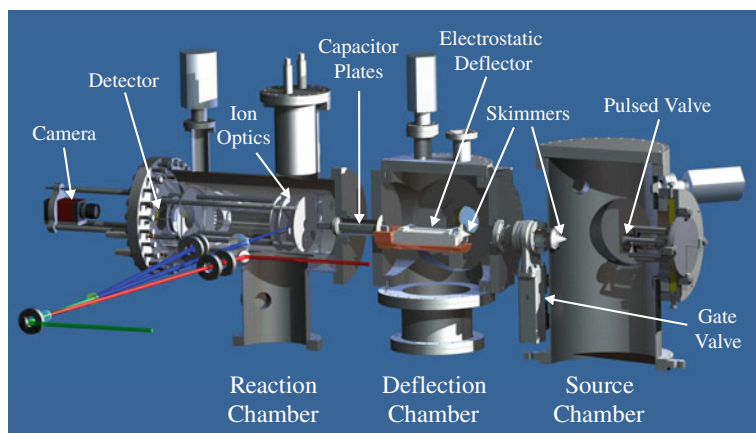
## 2.3 The Aarhus VMI Spectrometer

The Aarhus spectrometer was used in the study of the Coulomb explosion dynamics and torsional motion of the substituted biphenyl molecules 3,5-dibromo-3',5'-difluoro-4'-cyanobiphenyl and 3,5-dibromo-3',5'-difluoro-4-cyanobiphenyl presented in Chaps. 6 and 7. The experiment is located in the laboratory of Prof. Henrik Stapelfeldt at the University of Aarhus.

### 2.3.1 Overview

The experiment comprises three main vacuum chambers: the source chamber, the deflection chamber, and the reaction chamber. An illustration of the experiment is shown in Fig. 2.3. The molecular beam is introduced into the source chamber by way of a supersonic expansion through a high pressure Even-Lavie pulsed valve (see Sect. 2.3.2). The molecular beam is skimmed twice at distances of 14 and 38 cm from the nozzle in order to collimate the expansion. The first skimmer is located at the junction between the source and deflection chambers, and has a relatively large orifice (3 mm, Beam Dynamics Inc.) so as not to attenuate the signal too strongly. The second skimmer is fitted immediately before an electrostatic deflector and has a 1 mm orifice to ensure that the supersonic expansion is well collimated to form a cold molecular beam.

The molecular beam then travels through a 15 cm long electrostatic deflector (see Sect. 2.3.3), which acts to separate the molecules with respect to their rotational quantum states, thereby improving the degree of adiabatic alignment achievable using the nanosecond laser pulse.



**Fig. 2.3** A three-dimensional model of the Aarhus VMI spectrometer. The principal components are identified and labelled

The molecular beam then passes into the reaction chamber, which contains the ion optics assembly and the field-free drift region. The ion optics consists of three open electrodes, which act as an electrostatic lens. The first two electrodes are supplied with high voltages optimised to effect velocity-map imaging, while the third electrode is electrically grounded, which acts both to focus the ions and to isolate the field-free drift region from the potentials applied to the first two plates. The laser pulses enter the experiment through a fused silica window on one side of the reaction chamber, intersecting the molecular beam in a perpendicular manner between the repeller and extractor electrodes of the ion optics assembly. The ion optics and drift region are surrounded by a single cylindrical  $\mu$ -metal shield in order to isolate the spectrometer from external magnetic fields, which could influence the trajectories of the ions.

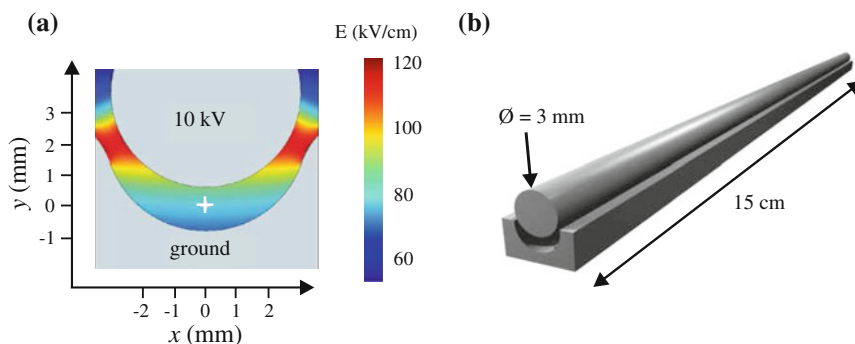
The ions are detected by a pair of chevron-stacked MCPs coupled to a P47 phosphor screen (EI-Mul Technologies Ltd., B050V, ScintiMax<sup>TM</sup>). The events on the phosphor screen are captured using a PImMS camera, which is described in detail in Sect. 2.5.

### 2.3.2 Molecular Beam Source

The molecular beam is produced by a supersonic expansion through a high pressure Even-Lavie pulsed valve (E.L.-7-4-2005-HRR) [4, 5]. The valve is mounted such that it can be translated in the  $xy$ -plane (perpendicular to the propagation direction of the molecular beam) relative to the skimmer. The temperature of the molecular beam has been measured previously to be on the order of 1 K [6]. The pulsed valve has a maximum repetition rate of 1 kHz, but this was limited to 20 Hz in the experiments described in this thesis due to the repetition rate of the Nd:YAG laser system used to align the target molecules (see Sect. 2.3.4). The valve incorporates a thermocouple combined with a resistive heater, which allows operational temperatures in the range of 30–250 °C. This allows the relative concentration of the sample gas to carrier gas to be optimised when sublimation of a solid sample is required to produce a gas-phase mixture. Solid samples are introduced to the valve on a small glass fibre filter, which is inserted into an internal sample reservoir.

### 2.3.3 Electrostatic Deflector

The deflection system is based on that of Chamberlain et al. [7] and comprises a polished rod-shaped electrode with a radius of 3.0 mm, which nests inside a trough-shaped electrode with an inner radius of curvature of 3.2 mm. The rod electrode is separated from the trough electrode by two 0.9 mm MACOR<sup>®</sup> spacers. The geometry of the deflector ensures that, when a large electrostatic potential is applied to the rod electrode (up to 10 kV), a field which is strongly inhomogeneous along the  $y$ -axis (vertical, perpendicular to the propagation of the molecular beam) but is almost



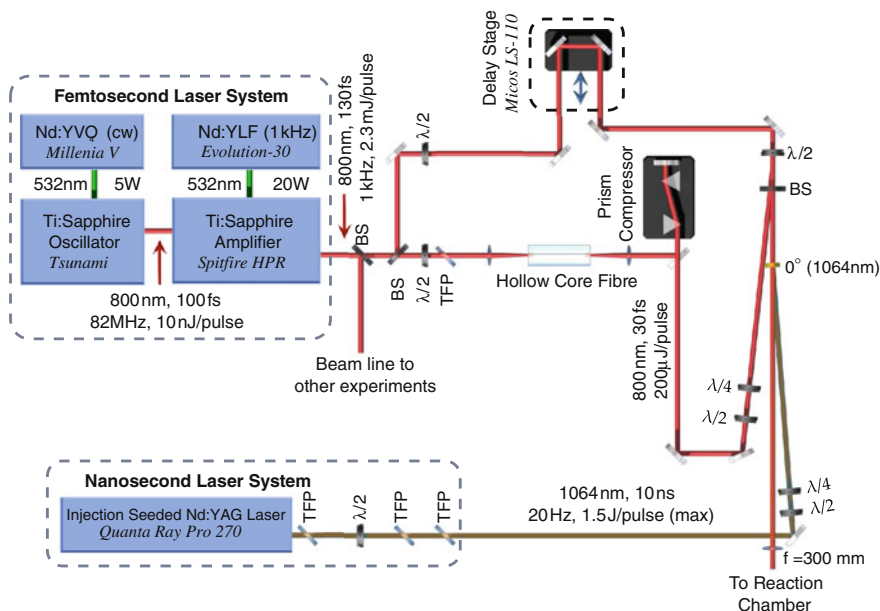
**Fig. 2.4** **Panel a** shows a cross section of the deflector, illustrating the electric field used to deflect the molecules according to their rotational quantum states. **Panel b** shows a three-dimensional illustration of the deflector. **Panel a** is adapted from Ref. [8]

perfectly homogeneous along the  $x$ -axis (horizontal, perpendicular to the propagation of the molecular beam) results. This is illustrated in Fig. 2.4a, where a colour scale is used to map the electrostatic field gradient between the two electrodes. Polar molecules entering the deflector therefore experience a force in the  $y$ -direction, due to the potential gradient, but not in the  $x$ -direction. The extent and direction of deflection of a molecule depends on its effective dipole moment, which is, in part, determined by the rotational quantum state of the molecule. The deflection system employed in this apparatus ensures that molecules in high-field-seeking quantum states are deflected upward, whereas those in low-field-seeking states are deflected downward. The molecules are therefore spatially separated in the  $y$ -direction according to the magnitude and direction of their rotation, thus resulting in prealignment of the target molecules. By focussing the laser beams into the appropriate part of the deflected molecular beam it is therefore possible to select molecules that are prealigned and rotationally cold.

The electrostatic deflector is immediately followed by a parallel plate capacitor comprising two 17 cm long polished stainless steel plates separated by two 2.7 mm MACOR<sup>®</sup> spacers. The plates are aligned parallel to the direction of deflection and ensure a non-zero potential gradient in the region between the electrostatic deflector and the electrostatic lenses of the ion optics assembly. The presence of a non-zero potential gradient helps to minimise Majorana transitions between individual M quantum states, which are degenerate in zero-field.

### 2.3.4 Optical Systems

The optical system comprises two main parts: a nanosecond Nd:YAG laser, used to adiabatically align the molecules; and a Ti:Sapphire femtosecond system, used to



**Fig. 2.5** Diagram of the optical systems coupled to the Aarhus spectrometer. See text for further details. Figure adapted from Ref. [8]

initiate torsional motion in the target molecules, and to induce non-resonant multiphoton ionisation and Coulomb explosion. An overview of the optical set-up is shown in Fig. 2.5.

### 2.3.5 Nanosecond Laser System

The nanosecond laser system consists of an injection seeded Q-switched Nd:YAG laser (Spectra-Physics, Quanta Ray Pro 270) with a maximum repetition rate of 20Hz and a maximum pulse energy of 1.5J. The laser is operated to output at the fundamental wavelength of 1064nm and has a pulse duration of 10ns. The pulses delivered to the experiment are attenuated to the desired energy ( $\sim 150$ mJ) following output by a combination of three thin film polarisers (TFPs) and a half waveplate (HWP). The first TFP is located immediately after the Nd:YAG laser system and acts to clean the polarisation of the laser output, whereafter the axis of polarisation may be rotated by a HWP. The HWP is followed by two further TFPs, with the extent of transmission being determined by the angle of the axis of polarisation of the incident light. A shift of  $0^\circ$  corresponds to full transmittance, whereas a shift of  $90^\circ$  corresponds to complete attenuation. The final TFP acts to clean the polarisation of the transmitted light. The final polarisation of the laser pulse is controlled by sending the beam through a further HWP and a quarter waveplate (QWP) prior to introduction into the reaction chamber.

The combination of low photon energy (1.17 eV) and long pulse duration relative to the molecular rotational period ( $\tau_{\text{YAG}} \gg T_{\text{rot}}$ ) makes these laser pulses ideal for adiabatically aligning [9] the target molecules prior to interaction with the femtosecond pump and probe laser pulses.

### 2.3.6 Femtosecond Laser System

The femtosecond laser system is based upon the output of a regenerative, chirped pulse amplified Ti:Sapphire laser comprising two main parts: an oscillator and an amplifier. The oscillator (Spectra-Physics, Tsunami) is pumped by the intra-cavity doubled output of a diode pumped Nd:YVO<sub>4</sub> cw laser (Spectra-Physics, Millennia V), providing an energy of >5 W at 531 nm. The Ti:Sapphire oscillator generates sub-100 fs pulses at a peak wavelength of 800 nm through Kerr lens mode-locking [10] at a repetition rate of 82 MHz, giving a pulse energy of <10 nJ.

The output of the oscillator passes into a Ti:Sapphire amplifier (Spectra-Physics, Spitfire-HPR) operating at 1 kHz, where it is regeneratively amplified in an optically excited Ti:Sapphire crystal. The amplification crystal is excited by the output of a 1 kHz Q-switched Nd:YFL laser (Coherent, Evolution-30) and provides amplification to energies of approximately 20 mJ at a wavelength of 527 nm. The repetition rate of the Nd:YFL laser limits the repetition rate of the amplification system to 1 kHz. Pulses entering the Ti:Sapphire amplifier are temporally stretched by positive Group Velocity Dispersion in a grating stretcher to avoid damaging the amplifier optics and must therefore be recompressed upon exiting the amplifier system. Recompression is achieved through a grating compressor, resulting in a final output of pulses with a peak wavelength of 800 nm, and a pulse energy of up to 2.3 mJ, at a repetition rate of 1 kHz. The amplifier output is then split into several beam lines by beam splitters, two of which are used for the pump (kick) and probe beam lines described in the following sections.

#### 2.3.6.1 Kick Pulse

The first femtosecond beam line ( $\sim 600$  mJ) is used to initiate torsional motion in the aligned biphenyl molecules. The 130 fs pulse duration produced by the Ti:Sapphire amplifier is sufficiently short compared to the torsional period of the biphenyl molecules ( $\sim 1.2$  ps) that it acts impulsively to induce coherent torsional motion across the ensemble of target molecules. In order that the time delay between the kick pulse and the probe pulse may be accurately controlled, the kick pulse is directed through a computer-controlled delay stage (Micos, LS-110). A HWP allows for control of the linear polarisation of the kick pulse. The power of the kick pulse is kept sufficiently low such that ionisation and subsequent Coulomb explosion of the target molecules is very unlikely.

### 2.3.6.2 Probe Pulse

The second femtosecond beam line is used to probe the molecular structure of the biphenyl target molecules through Coulomb explosion. In order that the deformation of the molecular skeleton is minimised on the timescale of multiple ionisation, the probe pulse must be short compared to the timescales of molecular motion. For this reason, it is necessary to temporally compress the probe pulse duration from the 130 fs output of the Ti:Sapphire amplifier. Compression also has the effect of increasing the intensity of the probe pulse, which is another prerequisite for achieving Coulomb explosion of the target molecules. The compression of the probe pulse is achieved in a two-step process. First, the beam is focussed by an  $f = 60$  cm lens into an argon-filled hollow core fibre mounted within a plexiglass tube at an overpressure of  $\sim 1.3$  bar. As the pulse travels through the hollow-core fibre, the process of self-phase modulation [10] causes the broadening of the spectral bandwidth of the pulse from  $\sim 10$  to  $\sim 50$  nm. Upon leaving the hollow-core fibre the beam is recollimated by an  $f = -100$  cm concave lens. The second step involves the temporal compression of the spectrally broadened pulse. This is achieved by passing the beam through a prism compressor, providing flat-phase pulses with a temporal width of 30 fs. Once focussed into the reaction chamber, the beam provides peak intensities of up to  $5 \times 10^{14}$  W cm $^{-2}$ , which is sufficient to induce Coulomb explosion of the target molecules. Before reaching the reaction chamber, the probe beam is passed through a HWP, allowing for control of the linear polarisation of the pulse.

### 2.3.7 Reagent Source

Gas phase samples of both 3,5-dibromo-3',5'-difluoro-4'-cyanobiphenyl (C $_{13}$ H $_5$ F $_2$ Br $_2$ N, DBrDFCNBph) and 3,5-dibromo-3',5'-difluoro-4-cyanobiphenyl (C $_{13}$ H $_5$ F $_2$ Br $_2$ N, DFDBrCNBph) were formed by heating less than 50 mg of solid sample to 170 °C in a high pressure atmosphere (90 bar) of helium within the internal sample reservoir of the Even-Lavie valve. Both chemicals are commercially unavailable and were synthesised specially for the experiment (for the procedure see the Appendix in Ref. [11]). It should be noted that the purity of DFDBrCNBph ( $\sim 99\%$ ) was determined to be superior to that of the isomer DBrDFCNBph ( $\sim 95\%$ ). The major contaminant found in the sample of DBrDFCNBph was identified as the byproduct in which both phenyl rings are F-substituted. Despite the higher vapour pressure of the impurity relative to that of DBrDFCNBph, it was not observed as a major contaminant in the ion images recorded. This is likely due to the larger deflection of the impurity by the electrostatic deflector causing its concentration in the interaction region to fall below detectable levels.

## 2.4 Velocity-Map Image Analysis

In a typical velocity-map ion imaging experiment, the three-dimensional product fragment Newton-sphere is projected onto a two-dimensional detector and the signal integrated over the time-of-flight coordinate. What results, therefore, is a two-dimensional projection of the full three-dimensional photofragment velocity distribution. Chapter 3 of this thesis explores an alternative approach to a variant of ion imaging that allows slices through the product fragment Newton-sphere to be extracted directly from the experiment, but in the more general case it is often necessary to invert the resulting two-dimensional image to recover the unintegrated velocity distribution of the nascent photofragments. The following sections provide a brief overview of the various approaches that have been developed to address this problem.

### Inverse Abel Transform

In the case of cylindrical symmetry, the most common approach to the problem of image inversion is to perform an inverse Abel transform [12] of the data to extract a representation of the meridional slice of the Newton-sphere. If  $P(x, z)$  is the two-dimensional projection of the three-dimensional distribution  $I(r, z)$  on the detector plane  $(x, z)$  then the two are related by the Abel integral [13],

$$P(x, z) = 2 \int_{|x|}^{\infty} \frac{r I(r, z)}{\sqrt{r^2 - x^2}} dr. \quad (2.1)$$

The quantity of interest is the laboratory frame distribution  $I(r, z)$ , which can in theory be evaluated from  $P(x, z)$  by the inverse Abel transform [14],

$$I(r, z) = -\frac{1}{\pi} \int_r^{\infty} \frac{[dP(x, z)/dx]}{\sqrt{x^2 - r^2}} dx. \quad (2.2)$$

While Eq. 2.2 describes precisely the relationship between the projected and laboratory frame distributions, it is unfortunately numerically impractical to handle directly. The most commonly used approach for solving the inverse Abel transformation is the Fourier-Hankel reformulation [15]. Unfortunately, the Fourier-Hankel method is notoriously sensitive to noise, which collects towards the central line of the reconstructed image, degrading the fidelity of the image inversion. A further issue is encountered when using the Fourier-Hankel method to reconstruct images that contain sharp, intense features, as these are often found to leave false artefacts in the inverted images, which are dependent on the exact Fourier-Hankel formulation employed.

### Alternative Approaches

An alternative to the inverse Abel transformation is the onion-peeling method [16], which inverts the image by treating the photofragment distribution as a series of concentric spheres. The algorithm proceeds by iteratively removing the contributions

from each ‘layer’ in turn, starting from the largest kinetic energy and progressively working towards the centre of the image. While relatively straightforward to implement and computationally inexpensive, this approach often leads to an overestimation of the contribution made by the fastest particles and is prone to cumulative error problems. For this reason, the experimental ion images are typically smoothed using a suitable algorithm before the Abel inversion is performed.

Rather than inverting the experimentally acquired ion images, the method of Vrakking [17] relies on a forward convolution of an assumed photofragment velocity distribution, which is then compared to the experimental data. The initial assumed distribution is iteratively refined until an acceptable agreement between the fitted image and the experimental image is achieved. This method introduces significantly less noise than the Abel inversion and onion-peeling methods, and has the advantage that the noise accumulates towards the centre of the image, rather than down the axis of polarisation, due to the polar formulation of the method. The obvious disadvantage is that some prior knowledge of the distribution must be assumed for the fit to converge at an acceptable speed.

### pBASEX

Perhaps the most successful approach to image inversion is that of Powis et al. [18], who have developed a method of solving the Abel inversion problem by fitting a set of radial forward basis functions that correspond to analytical inverse Abel transforms. The method is a reformulation in polar coordinates of the method of Dribinski et al. [19] and relies on fitting the kinetic energy distribution with a discrete number of Gaussian functions of a given width,  $\sigma$ . Within this approximation, the laboratory frame distribution may be described by

$$I(r, z) = \sum_{k=0}^{k_{\max}} \sum_{l=0}^{l_{\max}} c_{kl} f_{kl}(R, \Theta), \quad (2.3)$$

with

$$f_{kl}(R, \Theta) = e^{-(R-R_k)^2/\sigma} P_l(\cos \theta), \quad (2.4)$$

where  $\theta$  is measured with respect to the axis of cylindrical symmetry,  $P_l$  is the Legendre polynomial of order  $l$ , and  $R_n$  represents the mean radius of the  $n$ th radial Gaussian function. The method relies on fitting the experimental image to the Abel integrated versions of these basis functions to yield the radial and angular distributions of the nascent photofragments in the laboratory frame. As is also the case for the forward convolution method of Vrakking, the noise accumulates towards the centre of the inverted image, which is usually unimportant in image analysis. This method is known as pBASEX (polar basis set expansion), and is the primary image inversion algorithm used in the processing of the ion images presented in this thesis.

## 2.5 The PImMS Camera

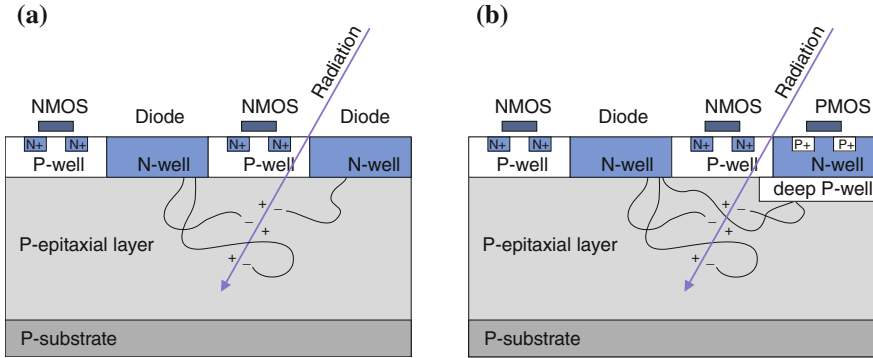
Central to the work presented in this thesis is the Pixel Imaging Mass Spectrometry (PImMS) Camera [20]. The device has been developed by a collaboration between research groups based in the Departments of Chemistry and Physics at the University of Oxford, and researchers working at the Rutherford Appleton Laboratory (RAL) in Harwell, Oxfordshire. The camera is a time stamping device based upon a complementary metal-oxide-semiconductor (CMOS) sensor incorporating novel INMAPS technology [21]. The device used in the work presented in this thesis was fitted with the prototype PImMS1 sensor, which has a resolution of  $72 \times 72$  pixels. A second generation sensor (PImMS2) with a resolution of  $324 \times 324$  pixels is currently in testing and will be available for experiments in the near future. This section describes the architecture, performance, and characterisation of the PImMS camera, preceded by a brief discussion of the principles behind CMOS and INMAPS technology.

### 2.5.1 CMOS Technology

Complementary metal-oxide-semiconductor (CMOS) technology was first developed in the 1960s and has since become very popular in a broad range of semiconductor applications. CMOS technology is found in a variety of imaging technologies, with applications in particle and nuclear physics [22, 23], X-ray medical imaging [24], electron microscopy [25], commercial digital cameras, and more recently in a variety of imaging mass spectrometry applications [26, 27]. The technology of monolithic active pixel sensors (MAPS) using CMOS technology has been advancing rapidly over recent years, with the notable development of INMAPS, where the ‘IN’ prefix stands for ‘Isolated N-well’. CMOS offers several advantages over the more conventional charge-coupled device (CCD) technologies traditionally employed in the manufacture of digital imaging sensors, such as reduced cost and power consumption. However, the principal advantage of CMOS over CCD technology for scientific applications lies in the ability of CMOS to support a large number of transistors on each pixel, providing valuable logic and processing power local to the light collection diodes.

#### 2.5.1.1 INMAPS

Figure 2.6 illustrates the principles of MAPS and INMAPS [21] CMOS technologies. In each case the CMOS wafer consists of a P-doped epitaxial layer supported on a P-doped substrate. Incident charged particles or photons create electron-hole pairs in the P-doped epitaxial layer, which act as minority carriers. The photoelectrons migrate to the N-doped diodes at the surface of the epitaxial layer, where they are collected. Since the photoelectrons are repelled by the small potential created at the

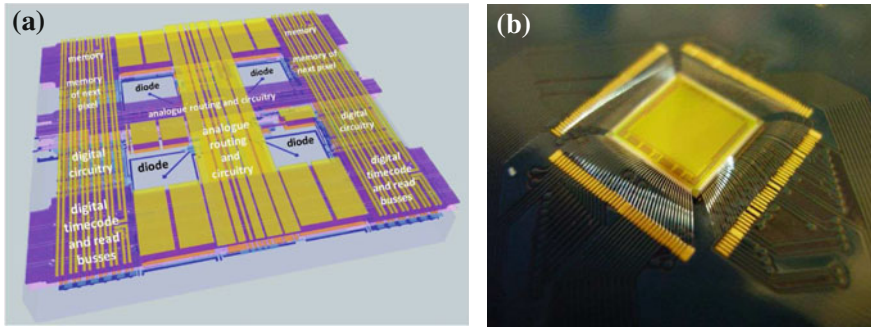


**Fig. 2.6** Diagram illustrating how radiation is detected by MAPS and INMAPS CMOS sensors. In the MAPS sensor, charge is collected by all N-type wells, limiting logic to NMOS transistors only. In the INMAPS sensor, the N-wells are shielded from the charge carriers in the P-epitaxial layer by a deep P-implant, allowing PMOS transistors to be included on the surface of the pixel. **a** MAPS. **b** INMAPS

junction between differently doped P-substrates, a 100 % collection efficiency by the diodes should be expected, provided the lifetime of the electron-hole pairs is long enough for them to diffuse to the P-N junction. A 100 % collection efficiency will, however, only be possible if the P-N junctions present in the pixel are exclusively those between the diodes and the P-epitaxial layer. This condition necessarily limits the electronics in the pixel to exclusively N-type (NMOS) transistors, significantly reducing the complexity of electronic processing that can occur on the pixel. INMAPS technology solves this problem of parasitic charge collection by P-type (PMOS) transistor supporting N-wells by inserting deep P-wells to shield the N-wells from the P-doped epitaxial layer. This allows the presence of both NMOS and PMOS transistors on the surface of the sensor, vastly increasing the electronic processing potential of each pixel in the monolithic array without reducing the charge collection efficiency.

### 2.5.2 PImMS Pixel Architecture and Functionality

The PImMS1 sensor comprises an array of  $72 \times 72$  pixels, each with dimensions of  $70 \times 70 \mu\text{m}$ , surrounded by the associated configuration and readout circuitry around the periphery of the chip. The sensor is mounted in a camera housing and light focussed onto the pixels using a commercial camera lens affixed to the camera body faceplate by either an F- or C-mounting fixture. The camera works on the principle of ‘time stamping’, wherein pixels independently record and store the value of an internal timer whenever an event with an intensity greater than a predetermined threshold level occurs. Each event recorded by the camera is therefore stored as a set of coordinates in  $x, y, t$  space, resulting in a compact data set containing the same

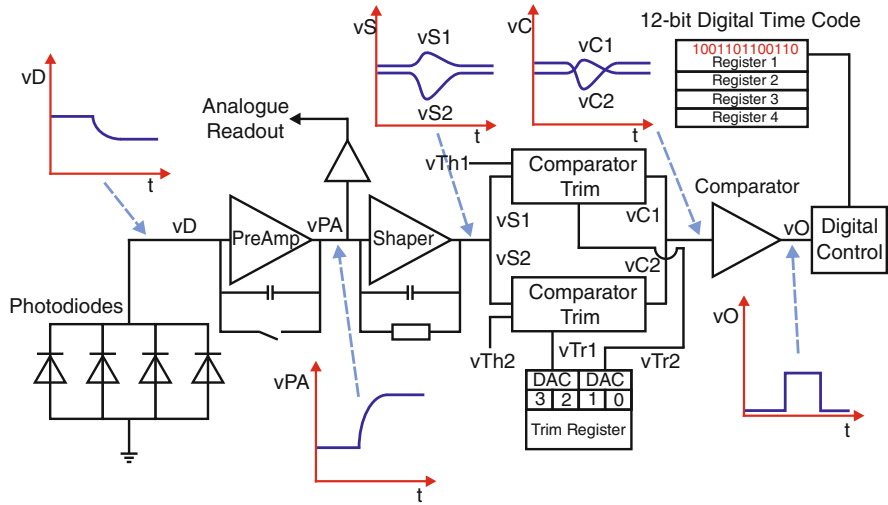


**Fig. 2.7** Panel a shows the PImMS pixel architecture, showing the four charge collection photodiodes and the supporting circuitry. Panel b shows a photograph of a PImMS sensor bonded to the sensor board. Adapted from Ref. [20]

information as afforded by frame-based imaging. This efficient approach to event-based image acquisition is made possible by the considerable processing power of each pixel. Each PImMS pixel contains over 600 individual transistors, a remarkably high number only permitted by the incorporation of INMAPS technology.

The pixel architecture is illustrated in Fig. 2.7, alongside a photograph of a complete PImMS1 sensor comprising an array of  $72 \times 72$  such pixels and the associated circuitry. Light is collected by four photodiodes contained within each pixel, corresponding to an active area of 16.9%. The remaining area of the pixel is occupied by the necessary onboard circuitry, which blocks the transmission of light to these regions.

Figure 2.8 shows a schematic of the pixel circuitry, illustrating the operation of the PImMS sensor. At the start of each acquisition cycle, an internal global 12-bit timer is triggered. The 12-bit timer permits the experimental period to be divided into 4095 equal time slices of width  $\geq 12.5$  ns. The value of zero is reserved to signify the absence of signal throughout the acquisition window. When a flux of photons from the phosphor screen impacts on a pixel, charge is collected by the four photodiodes, which is passed to an integrating pre-amplifier. The analogue signal is read out at this stage and integrated to give a measure of the total signal recorded by the pixel over the course of the acquisition window. A CR-RC shaper then produces two pulses representing the signal in differential form, which are passed to a comparator trim block. Since each pixel in the PImMS sensor is independent, each has a slightly different photon response curve. In order to provide a more consistent sensitivity over the whole sensor array, the response curve of each pixel may be shifted by four trim bits, allowing for 16 possible steps of adjustment. The comparator trim block applies this trim and thresholds the signal. The signal is then passed to a comparator, which determines whether an event over threshold has occurred. Positive events are then processed by the digital control logic, which stores the time code of the 12-bit global timer in one of four in-built 12-bit memory registers. At the end of an acquisition cycle, the data are read out from the memory buffers of the pixels and



**Fig. 2.8** Schematic of the PImMS pixel circuitry. See text for details

transferred to a PC via a USB 2.0 connection, where they are processed by custom built software (aSpect Systems). The data are stored as a list of events, with the data comprising the  $x$ - and  $y$ -coordinates of the pixel, the value of the 12-bit timer when the event was recorded, the acquisition cycle number, and the number of the register in which the event time stamp was stored. The PImMS1 camera repetition rate is limited by the USB data readout to a maximum of 550 Hz.

The data presented in this thesis were recorded using the PImMS1 sensor, which was designed as a prototype device and has a relatively modest pixel resolution when compared to conventional CCD cameras. The second generation (PImMS2) sensor has been developed during the course of this thesis and is currently undergoing testing. The PImMS2 sensor has a  $324 \times 324$  pixel array and offers a more precise calibration of the pixel-to-pixel sensitivity than the PImMS1 sensor through a more consistent trim response.

### 2.5.3 Post-Processing

The PImMS camera interfaces with a velocity-map ion imaging experiment by collecting signal in the form of photon flux from the phosphor screen. The performance of the device is therefore intrinsically related to the operating parameters of the MCP-phosphor detector, which must be optimised to yield the highest quality experimental data.

Each ion event, amplified by the MCPs, results in a cascade of electrons hitting the phosphor screen, causing a flash of light, which is detected by the PImMS camera.

Each flash on the phosphor screen typically illuminates several pixels, resulting in a cluster of pixels corresponding to each ion detected. The intensity profile of each flash on the phosphor screen is expected to be somewhat Gaussian, with a higher brightness towards the centre of the cluster, where the highest density of electrons impact upon the phosphor, and dimmer towards the edges of the cluster. For an event to be recorded, the charge build-up within the diodes of an individual pixel must be sufficient to exceed an externally chosen threshold value. Pixels that lie towards the centre of a cluster will be subject to a higher photon flux, and should therefore be expected to go over threshold at an earlier time than those towards the edge of a cluster. Since the earliest a pixel can detect an ion event is the actual time of the ion hit on the detector, the earliest time codes present within a cluster are necessarily the most accurate.

### 2.5.3.1 Centroiding

With these considerations in mind, the PImMS data were post-processed to reduce each cluster down to a single pixel and a single time code, a process known as centroiding. The centroiding algorithm identifies clusters through eight-fold connectivity (8 nearest neighbours), and determines the coordinate of the cluster centre through a weighted average of the coordinates of each pixel belonging to the cluster. The weighting factor for each pixel is determined by the time code of the event recorded, with earlier time codes corresponding to a larger weighting factor. In this way, the time code information is used as a surrogate for the absent intensity information. The event coordinate is given by

$$C = \frac{\sum_{i=1}^N r_i t_i^{-1}}{\sum_{i=1}^N t_i^{-1}}, \quad (2.5)$$

where  $r_i$  is the coordinate of the  $i$ th pixel and  $t_i$  is the time of the event, given by

$$t_i = T_i - T_0 + 1, \quad (2.6)$$

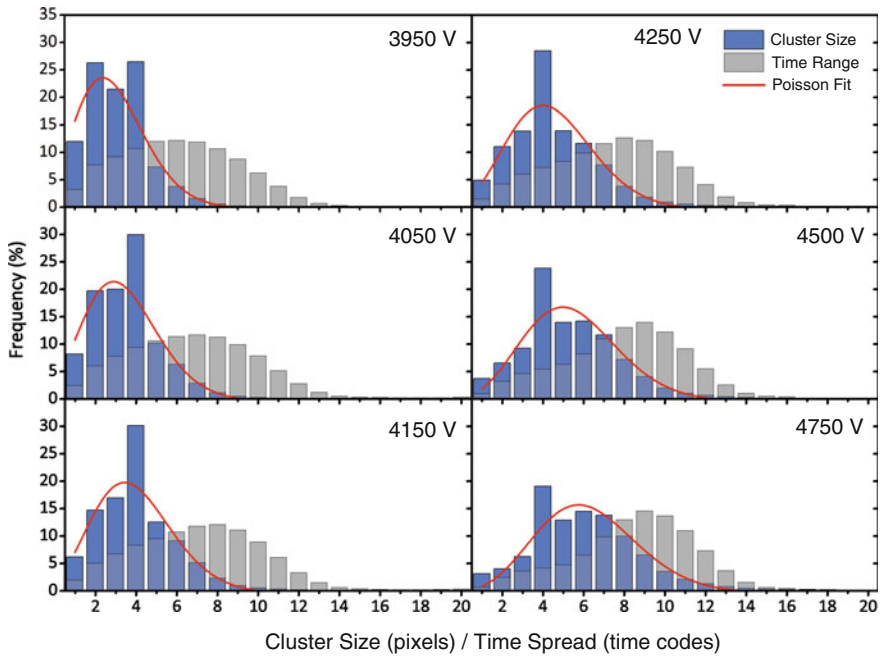
where  $T_i$  is the time code of the event and  $T_0$  is the time code of the earliest event recorded in the cluster.

Since recorded events occur with both a two-dimensional Cartesian coordinate and a time code, limits must be placed on the maximum temporal range of the events contributing to each cluster. The processing algorithm searches the data for events by working through the time codes sequentially from the first to the last. When an event is identified, the algorithm searches for further events spatially connected to the seed pixel by eight-fold connectivity and within a predefined number of time codes after the seed event, known as the ‘time window’. If further events fulfilling

these conditions are found, the algorithm continues to extend the search in the spatial domain using eight-fold connectivity, but retains the same limits on the maximum temporal range explored. When the algorithm fails to identify further events satisfying the required conditions of connectivity, the event coordinate is calculated using Eq. 2.5, and the time code of the event is taken to be  $T_0$ . Since the event coordinate is a non-integer value, it is possible to bin the events into a pixel array of greater finesse than that of the original sensor, thereby increasing the effective resolution of the device. This approach is known as ‘megapixeling’.

### 2.5.3.2 Cluster Characterisation

In order to optimise the centroiding algorithm, it was necessary to characterise the data recorded by the PImMS camera. Figure 2.9 compares data from several otherwise identical experiments, in which the MCP gain was kept constant and the phosphor voltage varied. The voltage across the MCPs was kept at 1750 V, with the voltage between the back face of the MCPs and the phosphor screen taking values in the

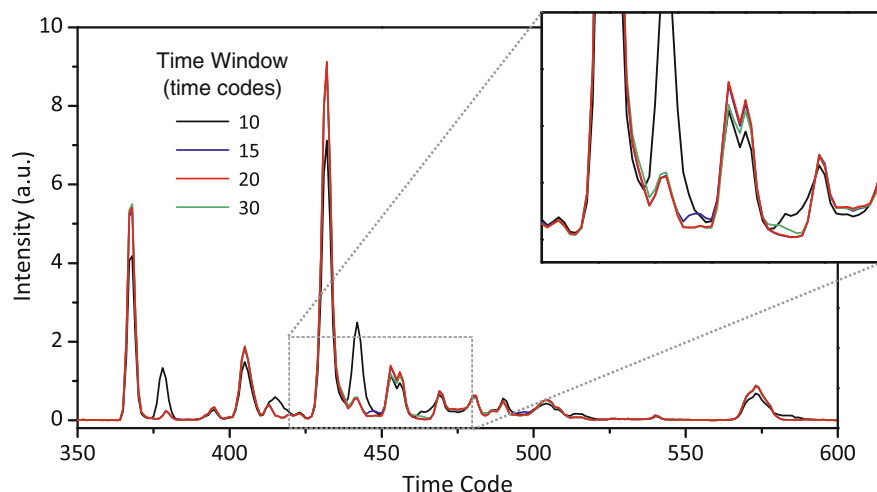


**Fig. 2.9** Histograms of the cluster size (blue bars) and the range of time codes present within a cluster (grey bars) for various phosphor screen voltages. The MCPs were operated with a potential of 1750 V across the two plates. The time spread is calculated as  $T_{\max} - T_0 + 1$ , where  $T_{\max}$  is the latest time code and  $T_0$  the earliest time code present in a cluster. The red curves are Poisson fits to the cluster size data

range 2200–3000 V. The ions detected are from the Coulomb explosion of a biphenyl molecule (see Chap. 6) and were accelerated by a potential of 7500 V applied to the repeller electrode. The data show that as the voltage bias between the MCPs and the phosphor is increased the average cluster size also increases. The general distribution in each case may be modelled reasonably well by Poisson statistics (red curves), as should be expected for a largely statistical process. Deviations from Poisson statistics are caused by averaging over a large fragment mass range ( $m = 1\text{--}80\text{ Da}$ ), and the sampling of approximately circular phosphor flashes on a square pixel array. The latter effect is particularly pronounced for clusters of 4 pixels in size, which are significantly over-represented in the data. This is thought to be caused by the favourable overlap between a circular phosphor flash and a  $2 \times 2$  pixel cluster.

Characterising the range of time codes present within a typical cluster is crucially important to the effective implementation of the centroiding algorithm. Figure 2.9 demonstrates that the maximum time range remains almost constant across all operating voltages at approximately 15 time codes (187.5 ns), with the distribution peaking towards higher values as the phosphor voltage increases. The observed time range is reasonably consistent with the decay lifetime of a P47 phosphor screen ( $\sim 70\text{ ns}$  [28]). This result suggests that it should be possible to apply a universal time window to the centroiding algorithm as the time range is characteristic to the camera, and not to the operating voltages of the detector.

The data in Fig. 2.9 suggest that a time window of 15 time codes should be sufficient to capture all pixels within the majority of clusters. To test this assertion, data from the Coulomb explosion of a biphenyl molecule were processed through the centroiding routine with different time windows applied. The resulting time-of-flight spectra are shown in Fig. 2.10. The data illustrate the two conflicting pressures on the centroiding algorithm: firstly, that the time window must be long enough that it is unlikely that any pixels belonging to a cluster fall beyond the maximum time code permitted, and secondly, that the time window is not so long as to cause a significant number of pixels belonging to later, distinct events becoming included in earlier clusters. Using a time window that is too short results in ‘ghost peaks’ appearing in the time-of-flight spectrum. These ghost peaks are caused by the trailing events within a cluster being missed by the algorithm and therefore being counted as separate clusters in their own right. This effect can be seen in the time-of-flight spectra processed with time windows of 10 and 15 time codes in Fig. 2.10. The ghost peaks are most pronounced following the most intense signals in the spectrum, and occur at a time afterwards corresponding to the length of the time window. These ghost peaks therefore move in the time-of-flight spectrum, depending on the length of the time window used, and are therefore easily identified. Conversely, if the time window used is too long, larger peaks in the time-of-flight spectrum have a parasitic effect on those that follow. This effect can be seen in the time-of-flight spectrum corresponding to a time window of 30 time codes in Fig. 2.10, in which the peak at approximately time code 455 is reduced in intensity due to the shadowing by the



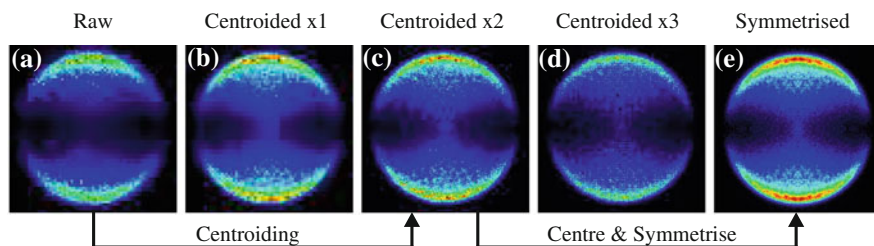
**Fig. 2.10** Time-of-flight traces following data processing using various ‘time windows’ in the centroiding algorithm, measured in 12.5 ns PImMS time codes. The time-of-flight spectrum is that recorded following Coulomb explosion of a substituted biphenyl molecule, as described in detail in Chap. 6. See text for details

intense signal centred on time code 430. After a careful analysis of the data, it was found that a time window of 20 time codes resulted in the optimum performance of the centroiding algorithm.

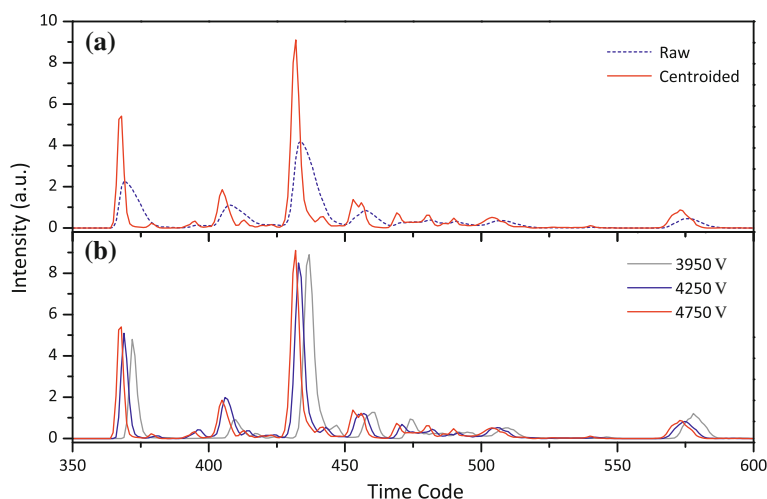
### 2.5.3.3 Centroiding Performance

Figure 2.11 illustrates the image processing scheme. The improvement in image resolution upon centroiding is clear, with each of the centroided images displaying a marked improvement compared to the raw data. Figure 2.11 also demonstrates the effect of megapixelising the data. It is clear that centroiding events to a pixel array with twice the original sensor dimensions does indeed afford an improvement in the spatial resolution. However, increasing the size of the pixel array beyond twice that of the original sensor does not seem to be beneficial as regular patterns begin to appear in the images. The arrows in Fig. 2.11 illustrate the processing scheme used for the images presented in Chaps. 3 and 4 of this thesis. The data are first centroided and the events binned to a pixel array with twice the dimensions of the original sensor ( $144 \times 144$ ). The centroided images are then centred and symmetrised appropriately along the horizontal and vertical axes ready for image analysis.

The images presented in this thesis that were recorded following the Coulomb explosion of substituted biphenyl target molecules (Chaps. 6 and 7) were not megapixelised or symmetrised due to the broader features of the ion images and the tendency of the fastest ions to overspill the detector in an asymmetric fashion. Instead, the data were centroided onto a  $72 \times 72$  pixel array and the resulting images



**Fig. 2.11** Panel **a** shows a raw image of the  $\text{I}^+$  ions resulting from the photodissociation of EtI at 245.36 nm (see Chap. 3 for details). Panels **b–d** show the centroided data binned into pixel arrays with dimensions of  $1\times$ ,  $2\times$ , and  $3\times$  that of the original sensor, respectively. Panel **e** shows the data in Panel **c** after centring and symmetrisation along the horizontal and vertical axes



**Fig. 2.12** Panel **a** compares the raw time-of-flight trace with that following centroiding of the data. Panel **b** compares the centroided time-of-flight spectra collected using three different phosphor voltages. The time-of-flight spectrum is that recorded following Coulomb explosion of a substituted biphenyl molecule, as described in detail in Chap. 6

smoothed using a moving average of the  $9 \times 9$  cluster centred on the pixel of interest in order to reduce the effects of incomplete data convergence and the variable pixel-to-pixel sensitivity of the PImMS sensor.

Panel (a) of Fig. 2.12 illustrates the effect of the centroiding algorithm on the time-of-flight information. The time-of-flight spectrum shown is that recorded following the Coulomb explosion of a biphenyl molecule, which is described in detail in Chap. 6. The broken blue trace shows the time-of-flight spectrum obtained by integrating over all pixels before post-processing, whereas the red trace shows the time-of-flight spectrum after post-processing. The improvement in the sharpness of the spectrum upon post-processing is striking; the broad features in the raw data are reduced to well-resolved mass peaks, with the full 12.5 ns time-resolution of the internal clock being utilised.

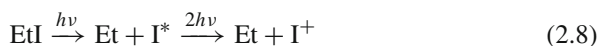
Panel (b) of Fig. 2.12 demonstrates the varying performance of the centroiding algorithm when using different phosphor voltages, while maintaining the same gain over the MCPs. In each case a voltage of 1750 V was applied across the MCPs, with a potential of 2200 V (grey), 2500 V (blue), and 3000 V (red) maintained between the MCPs and the phosphor screen. Upon increasing the voltage applied to the phosphor screen, the time-of-flight spectrum shifts to earlier time codes and noticeably sharpens. This is due to the increased brightness of the flashes produced by the phosphor screen upon increasing the kinetic energy of the electrons from the MCPs, which results in the threshold value of the PImMS pixels being exceeded at an earlier, and more accurate, time code. In order to maximise the time-resolution of the data, the detector was generally operated under conditions of high gain when interfaced with the PImMS camera.

### 2.5.4 Characterisation and Performance

The PImMS camera interfaces with a VMI spectrometer by simply replacing the standard CCD camera conventionally used to record images. While the PImMS camera significantly enriches the data available, the prototype PImMS1 sensor suffers from a relatively modest pixel resolution when compared to conventional CCD cameras. With this in mind, experimental images were recorded with both the PImMS1 camera and a conventional CCD camera (Photonic Science,  $576 \times 768$  pixels), and the parameters extracted from the images compared.

#### 2.5.4.1 Photodissociation of Ethyl Iodide at Around 245 nm

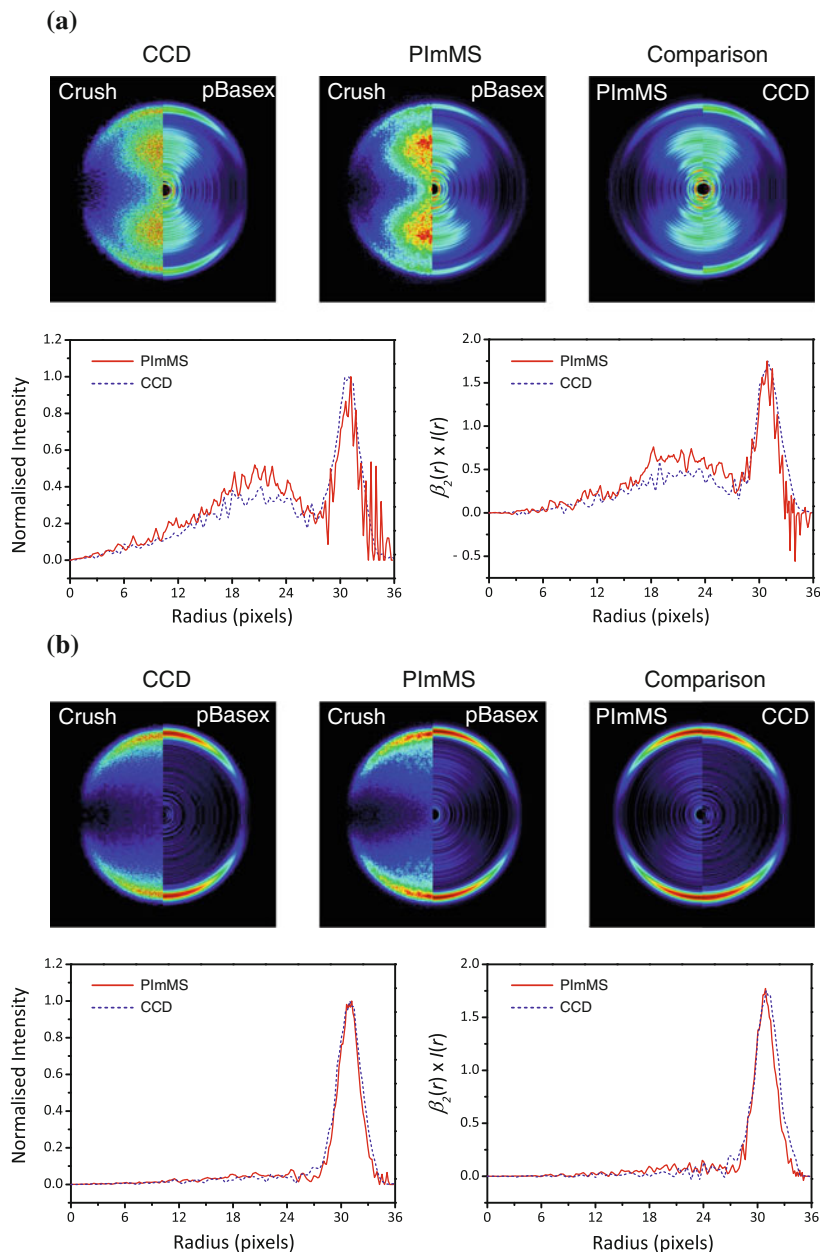
At around 245 nm, direct photodissociation is observed via the A band to form atomic iodine in either the ground ( $^2P_{3/2}$ ) or first excited ( $^2P_{1/2}$ ) electronic states [29]. The ground and excited state atomic photofragments may subsequently become ionised via either a three- or two-photon process, respectively, to form  $I^+$  ions:



Alternatively, EtI molecules excited to the A band may absorb a further photon, resulting in parent ionisation. Absorption of a further photon at the same wavelength results in bond fission to form neutral Et fragments and  $I^+$  ions:



At 245.00 nm the ion image consists of two principal components: a broad hourglass-shaped feature towards the centre of the image, and a narrower ring at higher



**Fig. 2.13** A comparison of the ion images recorded using the PImMS camera and a conventional CCD camera following the photodissociation of ethyl iodide at 245.00 and 245.36 nm. From *left to right*, the images presented are those recorded using the conventional CCD camera, the PImMS camera, and a comparison of the pBASEX inverted images collected using the two devices, as labelled. Beneath the images are the corresponding speed (*left*) and weighted anisotropy parameters (*right*), extracted using the pBASEX image inversion algorithm. See text for further details. **a** 245.00 nm. **b** 245.36 nm

fragment velocities (see Fig. 2.13). The sharp ring corresponds to two-photon ionisation of  $I^*$  photofragments resulting from the photodissociation of ethyl iodide via the  $A$  band (Eq. 2.7). The broad hourglass-shaped feature at lower fragment velocities has been assigned by Tang et al. [29] to dissociative ionisation of the parent molecule (Eq. 2.9). Ionisation of the ground state atomic iodine fragments produced following dissociation of ethyl iodide via the  $A$  band is not observed as this requires the absorption of a further photon, which is uncompetitive at the pulse energies used in these experiments.

At 245.36 nm a significant enhancement of the outer ring is observed, causing it to dominate the ion image. Since there are no resonant transitions from either the ground or first excited states of atomic iodine at this wavelength, this is proposed to be caused by a two-photon resonance from the  $I^*$  level to an auto-ionising electronic state, causing a significant enhancement of the ionisation probability of the excited state atomic iodine photofragments:

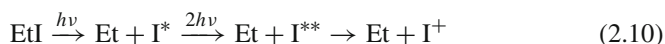


Figure 2.13 compares the images, velocity distributions, and anisotropy parameters measured at both 245.00 and 245.36 nm. The speed distribution and anisotropy parameters were extracted using the pBASEX algorithm, as described in Sect. 2.4. It should be noted that the anisotropy parameter ( $\beta_2$ ) has been multiplied by the normalised speed distribution in order to enhance the important features. The parameters extracted from both cameras are in good agreement. This result is perhaps surprising when it is noted that the pixel count of the CCD camera is almost two orders of magnitude greater than that of the PImMS1 sensor. The images taken at 245.36 nm are in almost perfect agreement, with the speed and angular parameters measured by the two devices almost indistinguishable from one another. The agreement at 245.00 nm is once again very strong, with a slightly different relative intensity of the features corresponding to the two product channels. This difference can be attributed to the fluctuating laser power in the experiment, causing differential enhancement of the two channels, and is not thought to be caused by any differences between the two cameras.

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