ULTRAFAST PROCESSES IN SMALL MOLECULES

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Abstract

The interaction of ultrafast ($6 \times 10^{-14}$ s) intense ($\sim 10^{15} - 10^{16}$ Wcm$^{-2}$) laser pulses with a number of small molecules is investigated. When focussed, the Ti:sapphire laser used in this work causes multiple ionization, resulting initially in dissociation, followed by Coulomb explosion into two or more energetic ionized particles. Ions generated by the Coulomb explosion are detected in a time-of-flight mass spectrometer. Computer controlled data acquisition and laser parameter control is effected through a graphical user interface. Covariance mapping is employed to identify ionization channels, a polarization comparison technique is used to quantify molecular reorientation, and an ion momentum imaging technique is developed, coupled with Monte Carlo simulations to measure the molecular geometry.

In water, the internuclear bonds double in length, in accordance with enhanced ionization theory. The molecule is also observed to straighten considerably, and the signature of laser-induced reorientation is observed. The geometry modification is interpreted in terms of bend angle softening, and comparisons with theoretically predicted reorientation rates are made.

In carbon dioxide, the ionization channels are identified, and a comparison is made with the results of other experiments. Laser-induced reorientation is observed, and quantified as a function of ionization channel. The bend angle distribution observed is compared with the expected zero-point distribution of the neutral molecule. Geometry modification in terms of light-dressed molecular potentials and the significance of stable molecular ions is discussed.

The Coulomb explosion of sulphur hexafluoride is investigated, and a comparison made with enhanced ionization theory. The explosion of this molecule is consistent with a single critical distance. (See Appendix.)

The dissociation and Coulomb explosion of the hydrogen molecular ion is investigated for the first time. Comparisons are made with previous experimental and theoretical results, and significant differences are observed, indicating the importance of the neutral molecule in the fragmentation process.
To my family.
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Chapter 1. Review of experimental and theoretical studies

1.1 Introduction

Recent advances in laser technology have lead to the routine availability of intense optical pulses on the same time scale as the vibrational motion of small molecules (Strickland and Mourou 1985, Squier et al 1991, Yamakawa et al 1991). These ultra-short pulses can then be focussed to generate electric field strengths comparable to the binding energy of the electron to the proton in the hydrogen atom. Such conditions have lead to the discovery of new highly non-linear phenomena in atoms and molecules.

Intense laser field interactions with atoms or molecules can be separated into two regimes, namely the multiphoton regime or the field ionization (or tunnelling ionization) regime. The distinction is made between the two regimes by way of the Keldysh parameter, \( \gamma \), (Keldysh 1965), which is defined as shown in equation 1.1:

\[
\gamma = \left( \frac{I_p}{2U_p} \right)^{1/2} \tag{Equation 1.1}
\]

where \( I_p \) is the ionisation potential (J), and \( U_p \) is defined as in equation 1.2:

\[
U_p = \frac{e^2 \varepsilon_0^2}{4m\omega^2} \tag{Equation 1.2}
\]

The quantity \( U_p \) is the pondermotive energy of an electron of charge \( e \) (C) and mass \( m \) (kg) in an electric field of maximum amplitude \( \varepsilon_0 \) (V/m), with frequency \( \omega \) (s\(^{-1}\)) and phase \( \phi \). The electric field \( \varepsilon(t) \) of the laser pulse is defined as shown in equation 1.3:

\[
\varepsilon(t) = \varepsilon_0(t) \cos(\omega t + \phi) \tag{Equation 1.3}
\]

For \( \gamma > 1 \), the ionization is in the multiphoton regime, where the atom or molecule absorbs several photons before ejecting an electron. In this regime, the ionization rate is proportional to \( I^n \), where \( n \) is the multiphoton order, and \( I \) is the maximum field intensity, as given by equation 1.4:

\[
I = \frac{c\varepsilon_0^2}{8\pi} \tag{Equation 1.4}
\]

where \( c \) is the speed of light. In the multiphoton regime, the electron has a small pondermotive energy, and as a consequence, the laser field may be treated as a
perturbation; this treatment is typical of high frequencies (e.g. UV, X-Ray).
However in the case where the pondermotive energy of the electron is greater then
the atomic ionization potentials, $\gamma < 1$, which applies if the tunnelling frequency of
the electron is less than the angular frequency of the oscillating electric field. In this
regime, the ionization is through the tunnelling of the ionizing electron through the
field-induced static potential barrier. Here, the potential barrier is the sum of the
Coulomb field and the electric field due to the laser. Ionization in the tunnelling
regime corresponds to longer wavelengths and higher intensities. In the tunnelling
regime, the action of the laser electric field on the Coulomb potential is no longer a
perturbation, hence multiphoton theory cannot be applied. However, the effect of the
laser field on the Coulomb potential can be modelled in a straightforward manner,
and has been found to successfully describe the tunnelling mechanism in atoms and
molecules (see for example Augst et al 1989). Importantly, the term 'field ionization'

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{Schematic representation of the behaviour of the outer electron in the field
of an atomic ion in (a) the multiphoton regime, (b) the tunnelling regime. The ionization
process has been successfully modelled by a classical over-the-barrier model (c).}
\end{figure}
is also used to describe the tunnelling regime, as the ionization process is dependent on the shape of potential created by the superposition of the laser field with the Coulomb potential. A comparison of the two different regimes is shown in figure 1.1.

1.2 Experimental investigations into the ionization mode in laser fields

The experimental investigation into laser-induced multiple ionization was instigated more than a decade and a half ago. The early experiments concentrated on the atomic inert gases. L'Huillier et al (1983a,b) measured the ionization rate of Xenon instigated by a 1064 nm wavelength laser, with a pulse length of 50 ps. In this study, it was concluded that, at high intensities, multiple ionization was a sequential process, and at low intensities, non-sequential.

The terms sequential and non-sequential describe the electron-removal mechanism, and are common to high-intensity laser studies in atoms and molecules. The definition of these processes is as follows.

- **Sequential ionization.**
  
  Sequential ionization implies that, during the laser pulse, electrons are removed in a step-wise manner, as indicated below for Xenon (equation 1.5a,b).

\[
\text{Xe} + nhv \rightarrow \text{Xe}^+ + e^- \quad \text{Equation 1.5a}
\]

\[
\text{Xe}^+ + nhv \rightarrow \text{Xe}^{2+} + e^- \quad \text{Equation 1.5b}
\]

- **Non-sequential ionization**

  In contrast to sequential ionization, non-sequential (or collective) ionization implies that two electrons are removed simultaneously, as shown in equation 1.6.

\[
\text{Xe} + nhv \rightarrow \text{Xe}^{2+} + 2e^- \quad \text{Equation 1.6}
\]

Counter to the conclusions of L'Huillier (1983), Luk et al (1983, 1985) reported non-sequential ionization of a range of atomic elements, including Xe, using a 193 nm ArF excimer laser with a 10 ps pulse length.

The first experiment using a molecular target as opposed to an atomic target was carried out in an effort to resolve the disagreements over sequential verses non-sequential ionization. Codling et al (1987) devised an experiment using hydrogen iodide (HI), which is isoelectronic with Xe. The molecule was multiply ionized by a 600 nm, 600 fs laser, the highest stage of ionisation observed was HI$^{6+}$. It was postulated that, if the ionization were non-sequential, the molecule would be ionized
Figure 1.2. Potential energy curves for hydrogen iodide as a function of internuclear separation. The dashed arrows represent non-sequential (direct) ionization, whereas the solid arrows demonstrate sequential ionization as the molecule dissociates six times, which would lead to a proton ($H^+$) and an $I^{5+}$ ion separated by the ground-state internuclear separation (1.61 Å). The two ions would then repel each other through the Coulomb interaction, and the proton would be emitted with a kinetic energy of around 45 eV. Conversely, if the ionization were sequential, the molecular ion would be ionized as it dissociated, hence the $H^+I^{5+}$ channel would be reached at a much larger internuclear separation, hence the proton would be observed with a far lower energy. This process is illustrated in figure 1.2.

The protons were observed to have a maximum kinetic energy of around 21 eV, hence Codling et al (1987) concluded that the ionization mechanism was sequential for hydrogen iodide, but at double the ground state separation, which implied sequential ionization also occurs for Xe for the same laser conditions.

In an earlier publication, Lambropoulos (1985) pointed out that an atom or molecule in an intense laser field will not be instantaneously exposed to the peak electric field, rather the temporal profile of the laser pulse will influence the rate at which ionization takes place. The results of Codling et al (1987) supported this conclusion. With the advance of laser technology, the focussed intensities generated increased,
thus allowing experiments to be performed in the tunnelling regime. In an important experiment by Augst et al (1989), multiple ionization of the noble gas atoms was studied in this regime. It was found that a classical field ionization model (see figure 1.1(c)) successfully predicted the appearance intensities of specific charge states. Figure 1.3 shows the results of this model in the ionization of noble gases. The ionization mechanism was approximated using the over-the-barrier method: as the laser field increases in strength, the electron can escape over the potential barrier directly into the continuum. In the case of Augst et al (1989) the effect of the electron tunnelling through the potential barrier was neglected. Even so, the agreement between the experimental results and the predicted appearance intensities is excellent.

![Figure 1.3. Field ionization model as applied to the noble gases (From Augst et al 1989)](image)

The first suggestion of applying a similar model to the multiple ionization of molecules was made by Frasinski et al (1987) in the case of N\textsubscript{2} and Codling et al (1987) in the case of HI. This model is referred to as the field ionization model. As in the atomic case, the outermost electron is situated in the sum of the Coulomb potential and the laser field. However, in transferring from the atomic case to the molecular case, a number of important differences exist. These were first reported in Frasinski et al 1987. Firstly, in the case of a molecule, the laser field acts over a finite distance (the internuclear separation) as opposed to over a point, hence the for
the same ionization potential, a molecule will be more easily ionized than an atom. This is illustrated in figure 1.4.

Secondly, it was observed that the laser polarization direction has a profound effect on the ionization process. Assuming linear polarization, the maximum electric field gradient occurs along the polarization direction. Initially, it was assumed that the molecules would have no time to rotate during the laser pulse (Frasinski et al 1987), and as a consequence, molecules that are initially aligned with the polarization direction should be preferentially ionized. Following their experimental investigations into N\textsubscript{2}, Frasinski et al (1987) concluded this was case.

1.3 Dissociative processes

Studies into the dissociative ionization of small molecules have focussed on the simplest molecular ion H\textsubscript{2}\textsuperscript{+}, hence this discussion will follow the literature. It has been assumed by a number of groups (Giusti-Suzor et al 1995 and references therein, Gibson et al 1997, Walsh et al 1998) that the first ionization step of the hydrogen molecule prepares the H\textsubscript{2}\textsuperscript{+} ion in accordance with the Franck-Condon principle, where the neutral molecule distribution of vibrational, rotational and translational states are transferred to the ion. It is also assumed (see references above) that the first
ionization step is very rapid as compared to dynamic effects in the molecule (reorientation, dissociation, and Coulomb explosion). In the following discussion, these assumptions are treated as reasonable.

It has been found that considering only the two lowest states of the H$_2^+$ ion ($1s\sigma_g$ and $2p\sigma_u$) gives a realistic framework within which to understand the dynamics of the system. See Giusti-Suzor et al 1995 for a summary of this principle.

Following the creation of the H$_2^+$ molecular ion, multiple photon absorption and emission can lead to a variety of complex phenomena. The most straightforward and physically transparent method to understand these processes is in terms of 'dressed' molecular potentials, as illustrated in figure 1.5.

![Figure 1.5](image_url)  
**Figure 1.5.** Ground state and first excited state potential of H$_2^+$ dressed by a photon field of 780 nm, where $\omega = 1.6$ eV. (From Giusti-Suzor et al 1995)

The 'dressed' molecular potentials are created by shifting the $1s\sigma_g$ and $2p\sigma_u$ levels down by the photon energy, $\omega$. This process is illustrated in figure 1.5 for the H$_2^+$ ion in 780 nm laser radiation. Assuming that the electronic wavefunction starts in one of the low lying vibrational states of the ion, figure 1.5 may be considerably simplified by observing parity rules, in that the electron wavefunction will only interact with those states of the same parity as the ground state (i.e. even). The dressed molecular potentials are therefore limited to the undressed $1s\sigma_g$ state, the
2pσ_u state dressed by one photon (2pσ_u + 1ω), the 1sσ_g state dressed by two photons (1sσ_g + 2ω) and the 2pσ_u state dressed by three photons (2pσ_u + 3ω). These potentials are shown in figure 1.6, again for 780 nm radiation. Importantly, these curves only apply below ~10^{11} \text{ Wcm}^{-2}, as they are the diabatic dressed potentials.

![Figure 1.6. Diabatic dressed potentials for H_2^+ dressed by a photon field of 780 nm, observing the selection rules.](image)

Above 10^{11} \text{ Wcm}^{-2}, the points at which the potentials cross (curve crossings) become repulsive, creating adiabatic dressed potentials, with associated 'avoided' crossings. These crossings are referred to by the number of photons required to dress the potential. For example, the avoided crossing between the 1sσ_g state and the 2pσ_u state dressed by three photons (2pσ_u + 3ω) is referred to as the three photon crossing or gap. In figure 1.7, the calculations of Giusti-Suzor et al (1995) are reproduced, showing the adiabatic dressed potentials for H_2^+ in a 780 nm 150 fs laser pulse for three different laser intensities.

The results reproduced in figure 1.7 are calculated using Floquet theory. The progressive pushing apart of the avoided crossings is analogous to the AC Stark shift.

The shapes of the adiabatic potentials are intensity dependent, and by careful consideration of the evolution of the avoided crossing and the populations of the
vibrational levels, new complex processes are found. In an analogy to above-threshold ionization (Gavrila 1992), the dissociative ionization of molecules by the passage of the vibrational population over (and in some cases through) the avoided crossings in the field-dressed potentials is referred to as above-threshold dissociation. The populations of the vibrational levels in the H$_2^+$ molecular ion are shown in figure 1.8. The dissociative processes found in H$_2$ are summarised in the following sections.

**Figure 1.7.** Adiabatic dressed potentials for H$_2^+$ in a 780 nm laser field at three laser intensities, illustrating the avoided crossings. (From Giusti-Suzor et al 1995)

**Figure 1.8.** Relative populations of the vibrational levels of H$_2^+$. 
1.3.1 Dissociative processes: one-photon dissociation or bond softening

Laser-induced bond-softening was initially proposed by Bandrauk and Sink (1981). The term "bond-softening" originates from the idea of the laser field progressively weakening the internuclear bond. As the laser field increases in strength, the one-photon adiabatic avoided crossing is suppressed, allowing lower and lower vibrational levels to dissociate with low kinetic energy.

The first observation of bond-softening was by Zavriyev et al (1990). Using the method discussed in section 1.3, figure 1.9 shows the potentials for the H₂⁺ molecular ion dressed in a 532 nm laser field. In the left-hand pane of figure 1.9, the arrow leading from the higher H₂⁺ vibrational levels to the one-photon dissociative limit shows the bond-softening process. As the laser intensity increases, the one-photon gap opens, allowing the vibrational levels lying above the gap to dissociate. The right-hand pane of figure 1.9 shows the experimental results of Zavriyev et al (1990). As can be seen, the bond-softening mechanism leads to a peak in the kinetic energy spectrum of H⁺ ions around 0.5 eV. The energy of the protons released in this process are measured with respect to the top of the adiabatic barrier, hence the kinetic energy is intensity dependent. Importantly, the first two peaks in the proton kinetic energy spectrum shown in figure 1.9 are separated by half the photon energy (1.3 eV) However, it should be pointed out that the supposed three-photon peak in the experimental results has not been reproduced since this publication.

![Figure 1.9](image)

**Figure 1.9.** Illustration of the three ATD paths open to the H₂⁺ ion exposed to 532 nm radiation. (Adapted from Zavriyev et al 1990)
1.3.2 Dissociative processes: two- and three-photon dissociation

While the higher vibrational levels of \( \text{H}_2^+ \) dissociate through the absorption of one photon, the lower levels can only be accessed through the absorption of more than one photon. This process is illustrated in figure 1.9 (left-hand pane) by the arrow starting in the \( v = 1 \) vibrational level, and initially following the three-photon adiabatic curve. Upon reaching the three-photon gap (around \( R = 4 \) au), the wavepacket can either continue along the dressed potential diabatically, and dissociate by sharing three times the photon energy, or can emit one photon and transfer adiabatically to the two-photon curve. As a consequence of the dissociation dynamics, the peaks in the kinetic energy spectrum of \( \text{H}^+ \) are referred to by the net number of photons absorbed. The results of Zavriyev et al 1990 (figure 1.9) were recorded with 532 nm pulses. Figure 1.10 shows results more applicable to the present work. Thompson et al (1997) used 750 nm 55 fs laser pulses to investigate the dissociation and Coulomb explosion of \( \text{H}_2^+ \). The one-photon (\( \omega_1 \)) and two-photon (\( 2\omega_1 \)) peaks are shown, along with the Coulomb explosion peak (1,1). Their results are qualitatively similar to those of Zavriyev et al 1990, however, Thompson et al (1997) observed no three-photon peak. As mentioned earlier, the three photon peak has not been observed in any other experimental studies. Given the maximum intensity in the studies of Zavriyev et al 1990, it is possible that the "3\( \omega \)" peak is actually a weak Coulomb explosion peak.

![Figure 1.10](image)

**Figure 1.10.** Kinetic energy spectrum from 55 fs 750 nm laser pulses at five laser intensities. (From Thompson et al 1997)
1.3.3 Dissociative processes: zero-photon dissociation

Giusti-Suzor et al (1992) proposed a mechanism in which high vibrational levels may become trapped in the adiabatic well above the one-photon crossing as seen in figures 1.7 (780 nm) and 1.9 (532 nm). The small portion of the wavepacket that lies above the diabatic crossing but to the right of the \( 2p\sigma_u + 1\sigma \) curve will be trapped as the laser field increases, and in certain cases, the adiabatic potential can increase to such a degree that the trapped population will escape with near-zero energy.

Very recently, Posthumus et al (2000) observed zero energy protons, and proposed that the molecule was behaving as predicted by Giusti-Suzor et al (1995). Posthumus et al (2000) referred to this process as zero-photon dissociation (ZPD), as there is no net photon absorption. The third harmonic (266 nm) of a Ti:sapphire laser were used to ionize \( \text{H}_2 \). Posthumus et al (2000) observed that ZPD is difficult to measure experimentally, as it requires very particular laser conditions, and efficient coupling between the one-photon crossing and the vibrational levels of the molecular ion.

Examining figures 1.7 and 1.8, in the case of 780 nm radiation, the vibrational levels high enough to be trapped by the upper well at the one-photon gap (\( v > 12 \)) have a very low population. By using the third-harmonic (266 nm), which is equivalent to a photon energy of 4.65 eV, the well-populated lower vibrational levels (around \( v = 5 \)) may be accessed by the upper well of the one-photon gap, hence allowing population transfer.

1.3.4 Dissociative processes: three-photon trapping

Zavriyev et al (1993) examined dissociative processes using 160 fs 769 nm laser pulses with intensities greater than \( 10^{13} \text{ Wcm}^{-2} \). The authors observed energetic protons with energies between 1 and 5 eV, as shown in figure 1.11. The kinetic energy spectra shown in figures 1.11(a) and (b) were recorded at intensities of \( 10^{15} \text{ Wcm}^{-2} \) and \( 2 \times 10^{15} \text{ Wcm}^{-2} \) respectively, and show evidence for structure. Zavriyev et al (1993) attributed the low energy peak around 0.5 eV to two-photon bond-softening peak. Compare these results with those of Thompson et al (1997) as shown in figure 1.10. Clearly, the intensities at which the experiments are performed are different, however, two major differences are observed. Firstly, in the results of Zavriyev et al (1993) (figure 1.11), no one-photon peak is present. Secondly, Thompson et al (1997) reported no structure in the Coulomb explosion peak, unlike
Zavriyev et al (1993). Importantly, the results shown in figure 1.10 were discussed in terms of enhanced ionization, which is discussed in detail later. The work of Zavriyev et al (1993) preceded the publication of enhanced ionization (Posthumus et al 1995, Zuo and Bandrauk 1995 and Seideman et al 1996), hence Zavriyev et al (1993) proposed another mechanism, involving trapping at the three-photon crossing.

The first step of the population trapping mechanism is illustrated in figure 1.12 for
H$_2^+$. Ionization of the neutral molecule was estimated to occur at $1.4 \times 10^{13}$ Wcm$^{-2}$, as shown in figure 1.12(a). The proton wavepacket then begins to move out along the $v = 5$ vibrational level. After 15 fs, the wavepacket reaches the other side of the potential well. After this time, the laser intensity has risen to $2.9 \times 10^{13}$ Wcm$^{-2}$, as shown in figure 1.12(b). At this point, the avoided crossing between the $1s\sigma_g$ state and the $(2p\sigma_u + 1\omega)$ state has not opened sufficiently to allow the wavefunction to escape, hence the wavepacket turns round and begins another oscillation. However, by the time the wavepacket reaches the turning point for the second time (after 40 fs, see figure 1.12(c)), the intensity has risen to such a degree ($9.0 \times 10^{13}$ Wcm$^{-2}$) that the three photon avoided crossing between the $1s\sigma_g$ state and the $(2p\sigma_u + 3\omega)$ state come into play. At this point, the wavepacket crosses into the new adiabatic well and is trapped.

The second step in the trapping mechanism proposed in Zavriyev et al (1993) involves multiphoton ionization of the population trapped above the three-photon gap. This process is illustrated in figure 1.13. Zavriyev et al (1993) calculated that

![Figure 1.12. A possible trapping scenario for H$_2^+$](Image)

The solid lines show the adiabatic dressed potentials, and the thin lines show the field-free potentials dressed by the photon energy ($\sim 1.6$ eV). (From Zavriyev et al 1993)
this process would require between 13 and 15 photons, depending on the position of the trapped vibrational wavefunction within the new potential. It is the state of the vibrational wavepacket in the upper three-photon gap that Zavriyev et al (1993) proposed caused the structure in the kinetic energy spectrum shown in figure 1.11. This conclusion has since been criticised by Thompson et al (1997), as the saturation intensity for the H$_2^+$ ion is $2 \times 10^{14}$ Wcm$^{-2}$ (c.f. $1.4 \times 10^{13}$ Wcm$^{-2}$ from Zavriyev et al 1993) is very similar to that at which (0,1) dissociation occurs, hence there will be very little time for the molecule to become trapped.

1.3.5 Dissociative processes - three-photon trapping continued: bond hardening

Very recently, Frasinski et al (1999) returned to the idea of population trapping above the three-photon crossing. The authors performed an elegant experiment using 792 nm laser pulses incident on H$_2$, and by varying the compressor grating separation to change the chirp of the laser pulse hence varying the pulse duration, were able to demonstrate the existence of three-photon trapping. The authors returned to the terminology of earlier works (Giusti-Suzor et al 1995) and referred to this process as bond-hardening, as the process stabilises the molecule against
dissociation, counter to bond-softening.

Frasinski et al (1999) observed a shifting of the one-photon peak in the proton spectrum when the pulse length of a $1.5 \times 10^{14}$ W cm$^{-2}$ laser pulse was varied from 45 fs to 540 fs. The results from this experiment are shown in figure 1.14. Clearly, if the laser pulse duration is increased, the pulse energy must also be increased to maintain a constant intensity.

![Figure 1.14. Bond-hardening manifests itself as a shift in energy of the one-photon peak as the pulse duration is shortened from 540 fs to 45 fs. (Adapted from Frasinski et al 1999)](image)


Frasinski et al (1999) described the bond-hardening mechanism in a similar way to vibrational trapping as discussed by Zavriyev et al (1993). The dynamics of this process are illustrated in figure 1.15.

The bond-hardening process essentially occurs in three phases. On the rising edge of the laser pulse (figure 1.15(a)), the vibrational wavepacket from the $v = 3$ or 4 levels in H$_2^+$ reaches the three-photon gap and can cross diabatically into the well created
Figure 1.15. The dynamics of bond-hardening. (a) On the leading edge of the pulse, the wavepacket crosses the three-photon avoided crossing. (b) As the intensity increases, the gap widens, trapping the wavepacket. (c) On the trailing edge of the pulse, the well flips from concave to convex, and the wavepacket is released. (Adapted from Frasinski et al 1999)

by the avoided crossing of the ground state and the three-photon dressed potential. The wavepacket may then oscillate once in this well, as shown in figure 1.15(b). However, by the time the wavepacket returns to the gap, the intensity has risen to such an extent that the probability of making the diabatic transition again is small. Bond-hardening is the trapping of the wavepacket in the adiabatic well. If this process happens early in the laser pulse, the wavepacket may be ionized by multiphoton absorption, as proposed by Zavryiev et al (1993). Frasinski et al (1999) proposed dissociation by a second mechanism. If the wavepacket survives until the trailing edge of the laser pulse, the well in which the trapping occurs switches from concave to convex, hence the wavepacket is then ejected onto the one-photon dissociative potential as shown in figure 1.15(c). The kinetic energy release associated with this process is related to the rate at which the laser intensity falls. The faster the decrease in intensity, the higher the wavepacket is lifted hence the greater the kinetic energy release.

1.4 Coulomb explosion processes
As introduced in section 1.2, the first ultrafast laser-molecule experiments were performed on HI to try to establish whether the electron removal was sequential (step-wise) or non-sequential (collective). Codling et al (1987) postulated that if the ionization mechanism were non-sequential, the ionized fragments would have a kinetic energy equivalent to the ions being placed at the ground state equilibrium.
separation, and allowed to mutually repel under the Coulomb interaction (Coulomb explosion). Conversely, if the ionization were sequential, the observed kinetic energy would be much lower, as the molecule would begin to dissociate, hence the final state of ionization would occur at a much higher internuclear separation.

The HI ionization results of Codling et al (1987) were not fully explained by either mechanism. The ions were detected with roughly half the expected kinetic energy, hence the molecule appears to have Coulomb exploded from double the equilibrium separation. This separation is referred to as the critical distance, as there appears to exist a critical separation at which ionization is dramatically enhanced.

The following sections will discuss the experimental results, leading to the idea of the critical distance (section 1.4.2). Classical and quantal theoretical treatments of the Coulomb explosion process are then considered.

1.4.1 Coulomb explosion processes - experimental results

Experiments performed over the last thirteen years have lead to the discovery of a number of new phenomena in molecules exposed to ultrafast laser pulses. These studies have centred on measuring the kinetic energy release (KER) from the laser-induced fragmentation of a wide variety of diatomic, triatomic and small polyatomic molecules. Rather than individually discussing this rather considerable number of publications, the results of these experiments will be tabulated, and the general behaviour commented on.

- Diatomic molecules


- Triatomic molecules

- Small polyatomic molecules

The following publications have investigated fragmentation in small polyatomic molecules: \( \text{C}_2\text{H}_2 \) (acetylene) by Cornaggia et al (1995), \( \text{C}_3\text{H}_4 \) (allene) and \( \text{C}_3\text{H}_8 \) by Cornaggia (1995).

All of these publications concluded that there existed a single distance for each molecule at which the ionization rate was maximised, and that this distance appeared to be independent of pulse length. The justification for the critical distance was the observation of a kinetic energy release between 40% (for \( \text{H}_2 \)) and 70% (for \( \text{I}_2 \)) of that expected if Coulomb explosion was occurring from the equilibrium separation. This is shown in table 1.1.

Table 1.1. Comparison between the equilibrium separation \( (r_e) \) and the experimentally measured critical separation \( (r_c) \) as observed in the Coulomb explosion of a range of molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( r_e ) (Å)</th>
<th>( r_c / r_e )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>1.1</td>
<td>0.4</td>
<td>Thompson et al 1997</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>1.1</td>
<td>0.43</td>
<td>Cornaggia et al 1991</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>1.1</td>
<td>0.47</td>
<td>Cornaggia et al 1991</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>1.21</td>
<td>0.42</td>
<td>Cornaggia et al 1991</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>0.96</td>
<td>0.48</td>
<td>Present work (ch 4)</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_2 )</td>
<td>1.2</td>
<td>0.5</td>
<td>Cornaggia et al 1992</td>
</tr>
<tr>
<td>( \text{Cl}_2 )</td>
<td>2</td>
<td>0.5</td>
<td>Schmidt et al 1994</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} )</td>
<td>1.13</td>
<td>0.38</td>
<td>Thomas 1999</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>1.16</td>
<td>0.51</td>
<td>See note (a)</td>
</tr>
<tr>
<td>( \text{HI} )</td>
<td>1.61</td>
<td>0.47</td>
<td>Hishikawa et al 1987</td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
<td>1.43</td>
<td>0.43, 0.57</td>
<td>Hishikawa et al 1998</td>
</tr>
<tr>
<td>( \text{OCS} )</td>
<td>1.16, 1.56</td>
<td>0.5</td>
<td>Goodworth 2002</td>
</tr>
<tr>
<td>( \text{I}_2 )</td>
<td>2.7</td>
<td>0.75</td>
<td>See note (b)</td>
</tr>
</tbody>
</table>

(a) This value represents the average of the results of Frasinski et al 1994, Cornaggia et al 1994, Cornaggia 1996 and the present work (chapter 5). Not taken into account are the results from Hishikawa et al 1999a.
(b) This value is the average over the results of Hatherly et al 1990, Cornaggia et al 1991 and the results reported in Posthumus et al 1995, 1996a and 1996b.

Schmidt et al (1994) reported that, in the case of a diatomic, the apparent internuclear separation at which the Coulomb explosion occurred from could be approximated using the following expression:

\[
R_e = 2.2(R_e)^{1/2} \quad \text{Equation 1.7}
\]

where \( q_1 \) and \( q_2 \) are the ionic charges and \( R_e \) is the equilibrium internuclear separation, all in atomic units. The measured kinetic energy release was converted to internuclear separation using equation 1.8:
where \( E \) is the total measured kinetic energy release in eV.

Schmidt \textit{et al} (1994) tried to explain these observation in terms of light-induced bound states, as introduced by Fedorov \textit{et al} in 1975. The term describes the stabilization of a molecule against dissociation. As discussed in section 1.3.4, Zavriyev \textit{et al} (1993) claimed to have observed population trapping in \( \text{H}_2^+ \) using 769 nm laser pulses with a duration of 160 fs. Schmidt \textit{et al} (1994) cited the work of Zavriyev \textit{et al} (1993) and Giusti-Suzor \textit{et al} (1992) to explain the observation that Coulomb explosion of chlorine occurred from an internuclear separation greater than the equilibrium separation. However, Schmidt \textit{et al} (1994) (along with Codling \textit{et al} 2000 and references therein) pointed out that it that it was difficult to conceive a mechanism which was independent of laser intensity, wavelength and pulse duration over a broad range of values. Importantly, the laser-induced stabilization model could not explain the stabilization of molecules up to ten-times ionized.

Around 1995, it became common to refer to the internuclear separation at which Coulomb explosion occurred as the 'critical' distance, as it appeared that there was an internuclear separation at which explosion occurred preferentially. A number of mechanisms were used to explain these observations, and they shall be discussed in the following sections.

1.4.2 Coulomb explosion processes - classical field ionization Coulomb explosion model

Posthumus and co-workers at the University of Reading, UK, developed a simple yet accurate model to predict the critical internuclear separation for diatomic molecules. Posthumus \textit{et al} (1995) analysed multiple ionization of diatomic molecules in a purely classical over-the-barrier treatment. Their field ionization, Coulomb explosion model predicts appearance intensities of ions originating from specific ionization channels, and allowed the calculation of the kinetic energies of the ionic fragments. Importantly, this model predicts the critical distance at which the ionization potential is maximised, and in agreement with experimental observations, these critical distances were independent of ionization channel.

In the model of Posthumus \textit{et al} (1995), the laser-molecule potential is modelled by
equation 1.9:

\[ U = -\frac{Q}{|x + R/2|} - \frac{Q}{|x - R/2|} - \varepsilon x \]  

Equation 1.9

where \( x \) is the distance along the internuclear axis, \( R \) is the internuclear separation and \( \varepsilon \) is the laser \( E \) field, and where

\[ Q = \frac{Q_1 + Q_2}{2} \]  

Equation 1.10

where \( Q_1 \) and \( Q_2 \) are the charges of the atoms. The energy level, \( E_L \), of the outer electron in this potential is approximated by:

\[ E_L = \frac{(-E_1 - Q_2/R) + (-E_2 - Q_1/R)}{2} \]  

Equation 1.11

where \( E_1 \) and \( E_2 \) are the ionization potentials of the atomic ions. This energy is the average of the ionization potentials and the influence of each charge across the internuclear separation.

In their 1995 publication, Posthumus et al defined the critical separation as the separation at which the energy level \( E_L \) touches both the inner and outer potential barriers. This is illustrated in figure 1.16.

As is apparent from equation 1.11, the only values required by this model are the atomic ionization potentials. Posthumus et al (1995) used this technique to estimate the critical separation of a wide range ionization channels for a number of diatomic molecules and for carbon dioxide, which was approximated as linear. The authors
found that the predicted critical separations did not vary substantially over the range of ionization channels produced, and agreed well with experimental observations. The results of these calculations are shown in figure 1.17; table 1.2 identifies the data in figure 1.17.

<table>
<thead>
<tr>
<th>Label</th>
<th>Publication</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Cornaggia et al 1992</td>
</tr>
<tr>
<td>(b)</td>
<td>Posthumus et al 1995</td>
</tr>
<tr>
<td>(c)</td>
<td>Schmidt et al 1994</td>
</tr>
<tr>
<td>(d)</td>
<td>Cornaggia et al 1991</td>
</tr>
<tr>
<td>(e)</td>
<td>Normand et al 1994</td>
</tr>
<tr>
<td>(f)</td>
<td>Hatherly et al 1994</td>
</tr>
<tr>
<td>(g)</td>
<td>Dietrich 1993</td>
</tr>
<tr>
<td>(h)</td>
<td>Hatherly et al 1990</td>
</tr>
<tr>
<td>(i)</td>
<td>Cornaggia et al 1996</td>
</tr>
<tr>
<td>(j)</td>
<td>Frasinski et al 1994</td>
</tr>
</tbody>
</table>

As is apparent from figure 1.17, the agreement between the model of Posthumus et al (1995) and experimental results published up to that point is good. However, this model does not account for the laser pulse length, nor stepwise electron ejection. To remedy this situation, Posthumus developed the model described above into the field-ionization Coulomb explosion (FICE) model.

1.4.2.1 FICE model - classical realisation of the critical distance.

The field-ionization Coulomb explosion (FICE) model of Posthumus et al (1996a,b)
used the same equations as the 1995 model (Posthumus et al 1995), as shown in equations 1.9 to 1.11. To explain the mechanics of the field-ionization Coulomb explosion model, the results of Posthumus et al (1996a) have been reproduced in figure 1.18, which illustrates the model as applied to the $I_2^+ \rightarrow I^+ + I^+$ channel.

At an internuclear separation of 5 au, the energy of the outer electron (see equation 1.10) is well above the central potential barrier, as shown in figure 1.18(a). An intensity of $5.3 \times 10^{13}$ Wcm$^{-2}$ is required to suppress the outer barrier to the energy level of the electron: see figure 1.18(b). At higher internuclear separations, the appearance intensity decreases for two reasons. Firstly, the electronic energy level, $E_L$ rises, and secondly, the electric field, now acting over a longer distance, is more effective at lowering the outer potential barrier. At $R = 7.5$ au, the central barrier rises above the energy level of the electron. At this point, a third process comes into effect, namely electron localization.

The electron is localized when the central barrier increases to such an extent that it is equal to or higher than the energy of the electron. When this occurs, the electron is constrained to one of the two wells created by the nuclei and the laser field.

When the electron is localized in the left hand well, the Stark shift increases the

---

Figure 1.18. Potential wells for $I_2^+$ at three different internuclear separations in an intense electric field, illustrating the calculation of the classical appearance intensity of the $(1,1)$ channel. In frames (a), (c) and (e), the equivalent laser intensity is $7.9 \times 10^{12}$ Wcm$^{-2}$. In frames (b), (d) and (f), the intensities are $5.3 \times 10^{13}$ Wcm$^{-2}$, $1.2 \times 10^{13}$ Wcm$^{-2}$ and $3 \times 10^{12}$ Wcm$^{-2}$ respectively. (From Posthumus et al 1996a)
electron energy by $+eR/2$. Similarly, when the electron is localized in the right hand well, the energy decreases by $-eR/2$.

The combined effect of electron localization and the Stark shift is indicated by the vertical arrows in figure 1.18(c) and (f). The effect of electron localization is to further lower the appearance intensity, as the electron in the left hand well is easier to ionize; in fact it now only requires $1.2 \times 10^{13}$ Wcm$^{-2}$ to cause ionization.

At internuclear separations greater than 10 au, the central barrier hinders ionization, and as a consequence, the appearance intensity increases again. The height of the central barrier increases as a function of $R$ as does the appearance intensity. The difference between the models published in Posthumus et al 1995 and 1996a is that the latter does not require the outer barrier to match the inner barrier.

The overall influence of the effects described above conspires to create a minimum in the appearance intensity as a function of internuclear separation. This minimum is therefore the critical distance, $R_C$. The critical distance is the point where the upper Stark level is at the same energy as the central and outer barriers (see figure 1.18(d)).

### 1.4.2.2 FICE model - appearance intensity as a function of internuclear separation.

Posthumus et al (1996a) used the method described in section 1.4.2.1 to calculate the dependence of laser intensity required to generate a certain channel (appearance intensity) as a function of internuclear separation. An example of such a curve is shown in figure 1.19. As can be seen, there is a pronounced minimum in the appearance intensity at around $R = 10$ au.

The physical processes behind the structure of figure 1.19 are indicated by the three vertical dashed lines. At the equilibrium separation ($R = R_E = 5$ au), the electron energy level $E_L$ (see equation 1.11) is well above the central barrier. As the internuclear separation increases, the appearance intensity falls as discussed earlier. Firstly, $E_L$ increases, and secondly, the laser field is acting over a larger distance, hence lowers the outer barrier further. At $R = R_L = 7.5$ au, the central barrier rises above the electron energy level, localizing the electron. At this point, the Stark shift comes into play, and the energy level in the upper well is lifted over the inner barrier, hence lowering the appearance intensity. The appearance intensity is minimised when the up-shifted electron energy level is the same height as the inner and outer barrier. Then, as the internuclear separation continues to increase, the central barrier...
begins to impede the up-shifted stark level, hence the appearance intensity rises again.

A subtle point of the work of Posthumus et al 1996a is that the up-shifted stark level (left hand well in figure 1.18) is not allowed to jump from far below the central barrier height to far above it at the point of realization. Instead, it is only allowed to rise to the top of the central barrier. Whether this is above or below the outer barrier is what governs whether ionization occurs.

1.4.2.3 Classical trajectory calculations

Posthumus et al (1996a) calculated the appearance intensities for the symmetric channels (1,1) to (5,5) for I$_2$. The asymmetric channels (1,2), (2,3), (3,4) and (4,5) were assumed to lie halfway between the corresponding symmetric channels. However, at large internuclear separations, averaging the atomic charges over the whole molecule is unphysical (see equation 1.9), hence the appearance intensity tends towards the higher channel between $R = 10$ and 15 au. The results of these calculations are shown as solid curves in figure 1.20.

The initial step in the Coulomb explosion of I$_2$ is assumed to be the removal of one electron, hence producing a dissociative state. Using the over-the-barrier approach, the appearance intensity for I$_2^+$ is calculated to be around $2 \times 10^{13}$ Wcm$^{-2}$. It is
Figure 1.20. Classical appearance intensities of the fragmentation channels of I$_2$ (full curves) and classical trajectories (broken curves). The laser parameters corresponding to each of the trajectory calculations are as follows: (a) 150 fs, $8 \times 10^{13}$ Wcm$^{-2}$ resulting in (2,2) channel, KER = 15.9 eV, (b) 400 fs, $5 \times 10^{12}$ Wcm$^{-2}$ resulting in (2,2) channel, KER = 14.1 eV, (c) 150 fs, $2.5 \times 10^{14}$ Wcm$^{-2}$ resulting in (4,4) channel, KER = 58.8 eV and (d) 400 fs, $1 \times 10^{15}$ Wcm$^{-2}$ resulting in (4,4) channel, KER = 35.9 eV. (From Posthumus et al 1996a)

assumed that this step occurs at the equilibrium separation ($R = 2.6 \text{ Å} = 5 \text{ au}$), as shown in figure 1.20. The molecular ion generated then begins to dissociate. The dissociative behaviour of the I$_2^+$ ion was approximated by the Coulomb explosion of a molecule sharing the single charge across both nuclei. Posthumus et al (1996a) used the following relationships to calculate the kinetic energy release (KER) in eV:

$$E = \frac{14.4Q_1Q_2}{0.529R} \quad \text{where} \quad Q_1 = Q_2 = 0.5 \quad \text{when} \quad 5 < R < 10 \text{ au}$$

$$E = \frac{14.4Q_1Q_2}{5.29} \quad \text{where} \quad Q_1 = Q_2 = 0.5 \quad \text{when} \quad R > 10 \text{ au}$$

Equation 1.12.

The experimentally observed KER of the (0,1) dissociation channel is reasonably well reproduced by these equations. Hatherly et al (1994) observed I$^+$ ions from the (0,1) channel with a kinetic energy of between 0.5 and 1.0 eV. As is shown in figure 1.21, this is a reasonable approximation.

With the dissociation mechanism established, the molecule was allowed to expand, and the molecule is monitored in steps of $\Delta R = 0.1$ au, and the time taken to travel this distance $t(\Delta R)$ is calculated using the following expression:
Figure 1.21. The treatment of the (0,1) dissociation channel as used by Posthumus et al (1996a).

\[ t(\Delta R) = \frac{1}{2} \left[ \frac{E - Q_1 Q_2}{R} \right]^{1/2} \int_{R_1}^{R_2} \frac{dR}{\sqrt{E - Q_1 Q_2}} \]  

Equation 1.13.

where \( \mu \) is the reduced mass of the molecule, \( R_1 \) and \( R_2 \) are the limits of the present step and \( E \) is the cumulative energy, all in atomic units. Note that this expression is not published in Posthumus et al (1996a,b), only in Thompson's 1997 thesis. During the time \( t(\Delta R) \), the laser intensity will have increased, hence the new intensity \( I \) is then compared with the known appearance intensities at that value of \( R \). If the appearance intensity is exceeded, ionization to the next channel occurs. The expansion of the molecule will then be fully Coulombic, in the (1,1) channel, hence the rate of expansion must be altered. This process is repeated until the laser pulse has finished.

Posthumus et al (1996a) used this method to calculate the classical trajectories as shown in figure 1.20 (dashed lines). Depending on the intensity and pulse duration of the laser pulse, the final Coulomb explosion channel reached is found by following the trajectory of the internuclear separation as a function of intensity and observing where it first crosses the appearance intensity curves.

Following trajectories (a) and (b) in figure 1.20 (150 fs, \( 8 \times 10^{13} \) Wcm\(^{-2} \) and 400 fs \( 5 \times 10^{13} \) Wcm\(^{-2} \) respectively), which both result in the (2,2) channel it can be seen that
the shorter pulse reaches the (2,2) channel at a smaller internuclear separation, hence resulting in a higher kinetic energy release. However, the difference in KER is small (15.9 eV as compared 14.1 eV), and may not be resolved experimentally.

There is a more pronounced difference in the case of the higher intensity processes resulting in the (4,4) channel. Trajectories (c) and (d) in figure 1.20 have laser conditions of 150 fs, $2.5 \times 10^{14} \text{ Wcm}^{-2}$ and 400 fs $1 \times 10^{15} \text{ Wcm}^{-2}$ respectively. In the case of the 150 fs pulse (c), the final channel is reached just before $R_C$, with a KER of 58.8 eV. The 400 fs pulse however, generates the (4,4) channel well past $R_C$, hence the process can be thought of as PDI of the (3,3) channel, as the molecule passes $R_C$ before reaching the (3,4) channel. This is in agreement with calculations for the (3,3) channel, resulting in a KER of 34 eV.

Posthumus et al (1996a) compared experimentally measured kinetic energy releases in $I_2$ recorded using 5 different pulse lengths. These results are shown in table 1.3, and generally show the success of the FICE model. The notable exception is the (4,4) channel at 400 fs, which appears to be PDI of the (2,2) channel rather than the (3,3) channel as predicted.

<table>
<thead>
<tr>
<th>Channel</th>
<th>Experimental KER (eV)</th>
<th>Theoretical KER (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55 fs</td>
<td>100 fs</td>
</tr>
<tr>
<td>(1,1)</td>
<td>4.9</td>
<td>4.8</td>
</tr>
<tr>
<td>(1,2)</td>
<td>9.7</td>
<td>8.9</td>
</tr>
<tr>
<td>(2,2)</td>
<td>17.6</td>
<td>16.5</td>
</tr>
<tr>
<td>(2,3)</td>
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<td>47.2</td>
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<td>(4,4)</td>
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<tr>
<td>(4,5)</td>
<td>75.6</td>
<td>72.3</td>
</tr>
<tr>
<td>(5,5)</td>
<td>94.0</td>
<td>88.5</td>
</tr>
</tbody>
</table>

1.4.3 Coulomb explosion processes - quantum mechanical treatments of enhanced ionization

The mechanics of multiple ionization of molecules by intense laser fields has been examined by a number of groups over the last decade. Plummer and McCann (1996) examined the ionization of $H_2^+$ in a static electric field, Corkum and co-workers have solved the time-dependant Schrödinger equation (TDSE) in one-dimension for a
generic diatomic (Seideman et al 1995, Ivanov et al 1996), and Bandrauk (Zuo and Bandrauk 1996) and co-workers have performed a three dimensional solution for H$_2^+$. Kawata and co-workers (1999) have expanded the work of Bandrauk using a different mathematical technique. All of these studies observed considerable enhancement of the ionization rate for internuclear separations greater than the ground state separation.

1.4.3.1 One-dimensional DC treatment of intense field ionization of H$_2^+$

Within the assumption that tunnelling ionization occurs very rapidly within the laser cycle, Plummer and McCann (1996) simulated the ionization of the H$_2^+$ molecular ion in a static field. The authors used a Floquet technique to calculate the energies and ionization rates of the 1s$\sigma_g$ and 2p$\sigma_u$ (referred to by the authors as 1$\sigma_g$ and 1$\sigma_u$) levels in static laser fields with intensity around $10^{14}$ Wcm$^{-2}$. Plummer and McCann (1996) found that the ionization rate from the upper level was considerably higher than from the lower level (except in very strong fields, where their model breaks down). The ionization rate from the upper level is shown in figure 1.22 as a function of internuclear separation. As can be seen in figure 1.22, there are two distinctive maxima in the ionization rate at around $R = 6$ au and $R = 10$ au. Plummer and

![Figure 1.22](image)

**Figure 1.22.** Static field ionization rate as a function of internuclear separation for H$_2^+$, where ionization occurs from the upper level (From Plummer and McCann 1996)
McCann observed that the first maximum at $R = 6$ au could be explained by over-the-barrier ionization of the upper level following the Stark shifting of the levels by the laser field. The authors could not explain the maximum observed around $R = 10$ au using this simple method. To counter this problem, Plummer and McCann (1996) calculated the ionization rates from the upper and lower levels during a time-averaged electric field (equivalent to a laser pulse envelope), and found that the three-dimensional propagation of the electron wavefunction from the upper level complicated the ionization process. By calculating the electron current as the molecule expands, Plummer and McCann observed that the "wavefunction of the upper level scattered from the lower well". They concluded that the $\text{H}_2^+$ system in an intense laser field required a full quantum-mechanical treatment.

1.4.3.2 One-dimensional AC treatment of intense field ionization in a diatomic molecule

Corkum and co-workers examined the experimental results suggesting the existence of a critical separation, and concluded that the stabilization model (Schmidt et al 1994, section 1.4.1) could not offer a satisfactory explanation. Seideman et al (1995), and more thoroughly, Ivanov et al (1996), took the field ionization model of Codling et al (1987) as their starting point. They modelled a generic diatomic molecule $\text{A}_2$, with characteristics similar to those of diatomic molecules such as iodine. Seideman et al (1995) created a smooth (no asymptotes at the nuclear centres) one-dimensional potential, representing the molecule aligned with the laser field, and solved the TDSE for an electron moving in this potential (hence within the single-active electron approximation). The Schrödinger equation was solved using the split operator fast Fourier transform method, and the nuclei were treated in the Born-Oppenheimer regime. The authors calculated the ionization potential as a function of internuclear separation for a number of Coulombic channels for two different sets of field conditions. Firstly, a smooth pulse $f(t) = 1 - \exp(-t/\tau)$ was simulated, to determine the ionization rates. The smooth turn on was necessary for the model to be physically realistic, and hence only populate the ground state of the field free molecule. Secondly, to determine the ionization probabilities, a short laser-like pulse 30 fs in duration with a wavelength of 900 nm was used. The results of these calculations are shown in figure 1.23(a) and (b) respectively.
As can be seen from figure 1.23, ionization is strongly enhanced for a range of critical internuclear separations. Figure 1.23(a) shows that enhanced ionization occurs over a wide range of channels, and that the peak in the ionization rate occurs at the same internuclear separation. Also, although the range of internuclear separation where enhanced ionization occurs with increasing charge decreases with channel, the peak value of the ionization probability remains very high as compared to the atomic case (when \( R \to \infty \)). In the case of the \( A_2^{3+} \) ion, the ionization rate is around three orders of magnitude greater than the atomic case. For the higher states, the enhancement is even higher. A small increase of intensity from \( 9 \times 10^{13} \text{ Wcm}^{-2} \) to \( 1.2 \times 10^{14} \text{ Wcm}^{-2} \) is required to produce \( A_2^{5+} \) ionization rates of the order of \( A_2^{\text{+}} \) at equilibrium. Qualitatively, Seideman et al (1995) observed a strong enhancement in the ionization rate of molecular ions around a critical separation, around double the
equilibrium separation, which is in good agreement with experiments. Seideman et al (1995) and Ivanov et al (1996) physically interpreted their results using a quasistatic model, which allowed for two major differences between the dynamics of atomic ionization as compared to molecular ionization. Importantly, Ivanov et al (1996) pointed out that earlier calculations of field ionization (Codling et al 1989) treated the electron adiabatically, whereas the model originally published by Seideman et al (1995) allowed the electron to move non-adiabatically. This difference is central to molecular ionization, when the shape of the potential is examined. Figure 1.24 shows the potentials used by Seideman et al (1995) and Ivanov et al (1996). The dashed arrow illustrates tunnelling ionization from the upper (left-hand) well. As can be seen, at small R (4 au, figure 1.24(a)), the electron must tunnel through the outer barrier, implying a low atom-like ionization probability. Similarly, at large R (16 au, figure 1.24(c)) the electron must tunnel through the central barrier. However, at intermediate R (around 8 au, figure 1.24b)), the central barrier narrows considerably, increasing the ionization rate.

Seideman et al (1995) realised the importance of the central barrier with relation to the behaviour of the electron in an oscillating field. Seideman et al (1995) and Ivanov et al (1996) observed that part of the electron wavefunction may become

![Figure 1.24](image-url)
localized in the rising well, and if a significant population is present in the well, it can tunnel through the central barrier into the continuum. This is where the non-adiabatic treatment of the wavefunction is necessary, because if the electron is treated adiabatically (low laser frequencies), the population transfers to the lower well, hence ionization is inhibited. The mechanism of localization of the wavefunction in the upper (rising) well is most efficient when the transition frequency (frequency of motion of the electron between wells) is smaller than the laser frequency.

Seideman et al (1995) also pointed out the presence of another ionization mechanism for high charge states at intermediate field strengths. For highly charged parent ions, the localized ground state in the rising well is very deeply bound, requiring a very strong field to suppress the outer barrier sufficiently. However, in the case of the highly charged parent ions, a number of localized excited states are supported by each well. Hence, during the first half-cycle of the laser field, the ground state of the rising well can become depopulated into the descending excited state by an adiabatic Landau-Zener transition. This is achieved by tunnelling through the central barrier between the two states. Similarly, as the two states come into resonance again, population may be transferred to the rising excited state by a diabatic Landau-Zener transition, which may then ionize through the central barrier when sufficient population has accumulated. This mechanism is referred to as resonant tunnelling.

Corkum and co-workers (Seideman et al 1995 and Ivanov et al 1996) concluded that molecular ionization proceeded in the following manner. Firstly, one or more electrons are removed until the first repulsive state is reached, then as the molecule expands, rapid multiple ionization may occur around the critical distance. This process stops when the molecule does not have time to expand to the next critical distance, or the laser pulse finishes. This effect causes the ion fragments from all channels to explode from around the same internuclear separation.

1.4.3.3 Three-dimensional AC treatment of intense field ionization of $H_2^+$

Bandrauk and co-workers have performed a number of calculations on the behaviour of simple one- and two-electron systems in intense laser pulses. Their efforts centred on solving the (TDSE) using split-operator numerical methods. Initial calculations were performed in the Born-Oppenheimer regime, and treated the nuclei and electron(s) in one-dimension. Later calculations were performed in three-dimensions.
and in the non-Born-Oppenheimer regime. The laser field was treated in a variety of ways, and the behaviour of the molecules was studied at a number of wavelengths (532 nm, 600 nm and 1064 nm).

Early efforts centered on understanding high-harmonic generation in H$_2$ and H$_2^+$, and were successful in reproducing experimental results. In two important publications, Zuo, Chelkowski and Bandrauk (1993) and Zuo and Bandrauk (1995) reported a significant enhancement in the ionization rate in H$_2^+$ as compared to atomic hydrogen over a specific range of internuclear separations. Zuo and Bandrauk (1995) named this phenomenon Charge-Resonance Enhanced Ionization (CREI) due to the importance of Charge-Resonance (CR) states that are strongly coupled to the laser field. The authors calculated the ionization rate of H$_2^+$ as a function of internuclear separation (R) for a 10$^{14}$ Wcm$^{-2}$ laser pulse at 1064 nm, by solving the TDSE at fixed R. In this case, the molecular ion is modelled in three-dimensions within the Born-Oppenheimer approximation. In this publication, the laser pulse was ramped linearly over 5 cycles (1 cycle = 17.5 fs) then kept constant. The ionization rate is calculated by allowing the electron wave function to propagate to the absorbing boundaries at the edges of the model.

The results of Zuo and Bandrauk (1995) are shown in figure 1.25. Two distinctive maxima in the ionization rate are observed, one at 7 au (R$_1$) and one at 10 au (R$_2$).

![Figure 1.25. Ionization rate of the H$_2^+$ molecular ion in a 10$^{14}$ Wcm$^{-2}$ 1064 nm laser pulse. The H$_2^+$ ion is modelled in three-dimensions in the Born-Oppenheimer regime. From Zuo and Bandrauk 1995)](image-url)
Zuo and Bandrauk (1995) attributed these maxima to electron localization ($R_1$) and CR-state-induced above-barrier ionization ($R_2$). The term 'Charge-Resonance' refers to the behaviour of the lowest two states of the $H_2^+$ molecular ion, namely the $1\sigma_8$ ground state and $1\sigma_6$ first excited state, in an intense laser field. Zuo and Bandrauk (1995) showed that these two states couple strongly to the laser field, and the dipole interaction between them diverges linearly as $R/2$ with large $R$. This causes the populations of these two states to become nearly identical and their energies to become nearly degenerate.

The ionization process identified by Bandrauk and co-workers involved the excitation of an electron in the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The laser field alters the energy of these states (discussed below). Ionization occurs when the LUMO lies above the inner and outer barriers, and the state is sufficiently populated.

Specifically, the CR effect is the shifting of the LUMO and HOMO by radiative coupling $Re/2$ (in au), along with the variation of the two levels with internuclear separation. This process is illustrated in figure 1.26, where the $H_2^+$ molecular ion is

Figure 1.26. Three-dimensional Born-Oppenheimer calculations of the LUMO (dotted line) and HOMO (dashed line) for $H_2^+$ as a function of internuclear separation in a static field of $10^{14}$ Wcm$^{-2}$ in a 1064 nm electric field. (From Bandrauk 1999)
modelled in a field of $1 \times 10^{14}$ Wcm$^{-2}$ at a wavelength of 1064 nm. For separations $4 < R < 10$ au, the LUMO is above all levels, but at $R > 10$ au, the LUMO is trapped by the central barrier. This causes the rise in ionization rate shown in figure 1.25. Between the equilibrium separation (2 au) and the first peak in the ionization rate (7 au), is analogous to electron localization (Seideman et al 1995, Ivanov et al, Posthumus et al 1996).

Around 8 au, the LUMO and HOMO are diabatically depopulated after half-cycles of the laser field. However, the population in the upper state increases substantially up to $R = 10$ au, hence the ionization rate rises, at which point the central barrier becomes degenerate with the upper level, hence ionization is inhibited.

Figure 1.27. (a) Relative energies of the outer barrier (thick solid line), inner barrier (thin solid line) and the upper (thick dashed line) and lower levels (thin dashed line). (b) Total electron population in the grid, showing the points at which ionization occurs. (Adapted from Kawata et al 1999)
Kawata and co-workers advanced the work of Bandrauk and co-workers after criticizing the numerical method applied (split operator method together with fast Fourier transformation), by applying a more advanced numerical technique, namely the alternating-direction method. They solved the TDSE for $H_2^+$ in three-dimensions in the non-Born-Oppenheimer regime for a more realistic laser pulse (10 fs, 884 nm, $3.2 \times 10^{14}$ Wcm$^{-2}$) as opposed to those used by Zuo and Bandrauk (1995). In Kawata et al. 1999 the motion of the electron wave packet was calculated during the oscillation of the laser pulse, and the energies and populations of the two lowest-lying states $1\sigma_g$ and $1\sigma_u$ are found. Kawata et al. (1999) calculated the behaviour of these two levels in relation to the height of the inner and outer barriers. The energies of the two levels and the heights of the inner and outer barriers are shown in figure 1.27(a) for the three-dimensional simulation. The population of the model grid is shown in figure 1.27(b), showing when ionization occurs. There is a small difference between the upper level rising over the outer barrier as the electron takes a finite time to propagate out of the grid.

Using this three-dimensional model, Kawata et al (1999) calculated the ionization probability of the $H_2^+$ ion as a function of internuclear separation. The authors used two starting points for the molecule, either in the $1\sigma_g$ ground state or the first excited

![Figure 1.28](image.png)

**Figure 1.28.** Ionization probability of $H_2^+$ as a function of internuclear separation. The open circles are when the simulated molecular ion starts in the ground state, and the closed circles are when the ion is in the first excited state (From Kawata et al. 1999)
state $1\sigma_u$. These results are shown in figure 1.28.

Comparing this result with that of Zuo and Bandrauk (1995) and Plummer and McCann (1996) as shown in figures 1.25 and 1.22 respectively, it can be seen that there is only one maximum in the ionization probability around $R = 7$ au. In the work of Plummer and McCann (1996), the peak around $R = 10$ au was understood in terms of the departing (ionized) electron scattering from the lower well, and in the work of Zuo and Bandrauk (1995), the maximum around $R = 10$ au was attributed to the charge-resonance effect. However, Kawata et al (1999) explained the maximum in the ionization probability around 7 au by barrier suppression coupled with high population of the upper levels by the diabatic transition of the electron wavefunction.

1.5 Laser-induced reorientation

A strong anisotropy in the angular distribution of the ionic fragments was observed in early experimental studies (Codling et al 1989, Hatherly et al 1990, Strickland et al 1992, Normand et al 1992, Dietrich et al 1993). In the case of diatomic molecules, it was found that the ions were preferentially ejected along the direction of the laser electric field. With the laser polarization parallel to the axis of the TOF spectrometer, pairs of 'forwards-backwards' peaks were observed, as discussed in chapter 2. However, when the polarization was rotated to be perpendicular to the TOF axis, the forward-backward peaks merged into one peak, centred at the zero momentum point. Initially, this observation was explained in terms of the classical field ionization model (see section 1.4), where it was argued that molecules initially aligned with the laser polarization direction would be more easily ionized than those at a large angle to the field. As the natural rotation of small molecules is of the order of picoseconds it was assumed that the molecules would be rotationally 'frozen' within the duration of the laser pulse. In the case of Codling et al 1987 and 1989, it was assumed only those molecules initially aligned with the field would be ionized, hence this process was referred to as 'preferential ionization'.

A number of publications addressed this problem. Strickland et al (1992) and Dietrich et al (1993) suggested that mechanism for laser-induced reorientation was that the electric field generated by the laser pulse would induce a dipole moment in the neutral molecule, which would then couple to the electric field of the laser. This
coupling produces a torque, which acts to align the molecule with the laser field. The following section will discuss the experimental investigations into laser-induced reorientation, followed by a brief summary of the theoretical treatment of this phenomenon.

1.5.1 Laser-induced reorientation - experimental results

Hatherly et al (1990) employed covariance mapping to measure the angular distributions of the ionic fragments from the Coulomb explosion of carbon monoxide, and observed that the angular distributions of the ionic fragments narrowed with increasing charge state. The authors concluded that this narrowing implied greater alignment with the laser polarization direction.

Strickland et al (1992) reported similar results after measuring the angular distribution of Coulomb explosion products from I₂ exposed to sub-100 fs pulses. The angular distributions showed strong alignment of the molecules with the laser electric field direction. As with Hatherly et al (1990), the higher the charge state, the greater the degree of alignment. An important argument was raised in Strickland et al (1992), in that the field ionization model could not account for the lack of ions emitted perpendicular to the polarization direction.

As discussed in section 1.4, there is a distribution of intensities within the laser focus. Clearly, the highest intensities will be produced at the centre of the focus. Furthermore, in accordance with Codling et al (1987) (see section 1.3), well aligned molecules are easier to ionize, hence well aligned molecules at the laser focus should produce the strongest decay channels. In the case of Strickland et al (1992), the highest decay channel observed was the (3,3) channel. However, there will also be molecules in the centre of the focus which are not well aligned, hence should ionize and Coulomb explode into lower channels. If this were the case, it was argued that there should be a broadening of the angular distributions as a function of peak laser intensity, and that ions should be detected at right angles to the polarization direction. As this effect was not observed experimentally, Strickland et al (1992) suggested that the laser field could be applying a torque to the molecules, causing reorientation of the unaligned molecules. The proposed mechanism for this reorientation was coupling of either an induced or permanent dipole moment with the laser electric field, which would produce a torque if there were any angle between the polarization and the 'dominant' dipole moment.
Thus, between 1990 and 1992, there was considerable debate as to the behaviour of molecules in intense fields. Codling et al (1987, 1989) believed aligned molecules were ionized, and unaligned molecules were not, whereas Strickland et al (1992) believed the molecules were forced into alignment, then ionized.

Normand et al (1992) performed an elegant pump-probe experiment in an attempt to resolve which mechanism was occurring. In this experiment, the dissociative ionization of carbon monoxide was studied using two linearly polarized 30 ps laser pulses, one polarized parallel to the detector axis, and one perpendicular. The two pulses were temporally separated by 800 ps; this period was chosen such that there was insufficient time for the random thermal motion of the molecules at room temperature to repopulate the focal volume following the action of the first pulse. The results of this experiment are shown in figure 1.29. If the hypothesis of Codling et al (1987, 1989) were correct, the TOF spectrum shown in figure 1.29(c) should be the sum of figures 1.29(a) and (b). However, this is clearly not the case. The number

![Figure 1.29.](image)

Figure 1.29. Ion time-of-flight spectra for pump-probe ionization of carbon monoxide with (a) perpendicular pulse only, (b) parallel pulse only and (c) the perpendicular pulse followed by the parallel pulse with a 800 ps delay. A schematic of the pulse delays is shown to the right of the figure, where the detector axis lies up the page. (Adapted from Normand et al 1992)
of ions produced by the second (parallel) pulse has been dramatically reduced by the action of the first pulse. Therefore, the first laser pulse is interacting with all of the molecules in the focus, causing reorientation then ionization, hence when the second pulse arrives, there are fewer molecules which can be ionized. However, because of the long delay between the pump and probe pulses, molecules within the focus that are not ionized in the first pulse have ample time to rotate, hence redistributing the population of aligned molecules.

Dietrich et al. (1993) performed a similar pump-probe experiment in I₂, but with far shorter pulses, more applicable to the current work. In this experiment, two orthogonal 70 fs pulses were used to field ionize iodine, chosen for its high moment of inertia, which prevents the natural rotation of the molecule being a significant factor. Experimentally, it was shown that the presence of the first pulse reduced the effect of the second pulse, as in Normand et al. (1992). Dietrich et al. (1993) came to the conclusion that the first laser pulse was reorientating the molecules, so when the second pulse arrived, the molecules in the focus were misaligned, hence decreasing the field strength experienced along the molecular axis. The authors suggested that the electric field of the laser could impart angular momentum to the molecules, which would cause the ions from the exploding molecules to be deflected significantly. They simulated the interaction of the ions with the laser field, and showed that the angular momentum imparted could deflect the ions. Figure 1.30 shows a comparison between the experimental results and the theoretical

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**Figure 1.30.** Angular distributions from the dissociative ionization of I₂ in an 80 fs laser pulse. The squares are the ion yield of the (1,2) channel and the solid line is a \( \cos^2\theta \) fit. The dashed line is a simulation of the ion yield if the laser field causes the ions to follow curved trajectories after dissociation. (From Dietrich et al., 1993)
calculations. The main difference between the results of Normand et al (1992) and Dietrich et al (1993) is that in the former, the reorientation is proposed to have occurred within the laser pulse whereas the latter concluded that the reorientation process could continue for up to 10 ps after the laser pulse.

The Coulomb explosion of diatomic molecules has been more recently re-examined by Posthumus et al (1998) who measured the angular distribution of the ionic fragments as a function of laser intensity. The field-ionization Coulomb explosion model was used in two dimensions to investigate the influence of angle-dependent enhanced ionization on the angular distributions. The authors calculated the threshold intensities for ionization into a range of channels for a series of angles between the laser polarization direction and the molecular axis. This result is shown in figure 1.32. They showed that, for a particular peak intensity (in this case, \(5 \times 10^{13}\) W/cm\(^2\), indicated by the horizontal dashed line), molecules perfectly aligned with the laser polarization originate from a low intensity volume of the focus. However, molecules that are initially badly aligned with the laser polarization have to lie nearer the centre of the laser focus to ionize into the same channel. This process is illustrated in figure 1.31 for the (1,2) channel. The arrow labelled (1) in figure 1.31 shows the range of intensities which generate the (1,2) channel from molecules that are perfectly aligned. This process will occur away from the centre of the focus. Molecules at an angle of 45° to the polarization will come from volume (2), which

![Figure 1.31](image-url).

**Figure 1.31.** The minimum threshold intensities at the critical distance \(R_c\) which define the fragmentation shells in the focal volume. The arrows show the shells in which molecules that make a certain angle with the laser polarization that end up in the (1,2) channel. (From Posthumus et al 1998)
must lie nearer the focus, hence contains fewer molecules. Molecules at an angle
greater than $74^\circ$ (3) to the field cannot contribute to the (1,2) channel. Posthumus et al (1998) calculated the relative signal from each of these shells, assuming an initial
random distribution of orientations. They showed that the predicted and observed
distributions were very similar, implying that, in the case of iodine, it was not
necessary to include any laser-induced reorientation effects to reproduce the
observed angular distributions. Furthermore, the broadening of the angular
distributions with increasing laser intensity was observed for iodine, as predicted by
Comparisons were also made between this classical model and the angular
distributions from hydrogen and nitrogen. Previous measurements on H$_2$ were
carried out above the saturation intensity ($2 \times 10^{14}$ W cm$^{-2}$) (Thompson et al 1997)
hence, these measurements were carried out below saturation. For both hydrogen and
nitrogen, Posthumus et al (1998) observed a narrowing of the angular distributions
with increasing laser intensity. A comparison between the results for iodine, nitrogen
and hydrogen is shown in figure 1.32.

![Figure 1.32](image-url)

**Figure 1.32.** The angular widths of the explosion channels of different molecule species as a function of laser intensities. The lack of laser-induced reorientation in iodine is shown by the agreement between the experimental results and the classical model. Nitrogen and hydrogen however, are reoriented by the laser. The narrowing of the angular distributions with increasing laser intensity is a signature of laser-induced reorientation. (From Posthumus et al 1998)
Ellert et al (1998) suggested a straightforward method for measuring whether a molecule is reorientated within the laser pulse. A comparison was made between TOF spectra recorded with circular and linear polarization. Importantly, for this technique to work, the energy in the circularly polarized pulse is made to be double that in the linear pulse and the linear polarization direction is parallel to the detector axis. Hence, in both cases, the average electric field in the direction of the detector is identical. If the angular acceptance of the detector is small, energetic ion fragments

![Graphs showing Coulomb explosion products from (a) oxygen, (b) chlorine and (c) iodine with linear and circular polarizations. The average electric field strength in the direction of the detector has been made the same in all three cases. The increase in ion signal with parallel polarization indicated laser-induced reorientation in the case of oxygen and chlorine. However, in the case of iodine, the ion signals are equal, implying there is no reorientation. (From Ellert et al 1998)](image_url)
reaching the detector originate from molecules that are well aligned when they
Coulomb explode. By investigating the ionization of CH$_2$I$_2$ with an 80 fs laser pulse
with linear and circular polarizations as described above, the authors showed that the
ion signal from circular polarization is nearly the sum of the perpendicular and
parallel components. This implies that the assumption of the equivalence of circular
and parallel polarizations with equal parallel field is well founded. Therefore, by
comparing TOF spectra recorded with circular and parallel polarizations (with equal
parallel components), any laser-induced reorientation will be apparent as an
enhancement of the ion signal in the parallel case. Ellert $et$ $al$ (1998) examined the
Coulomb explosion of a number of diatomic molecules under these conditions. The
results are shown in figure 1.33 (a-c) for oxygen, chlorine and iodine respectively.
There is clear evidence for laser-induced reorientation in the cases of oxygen and
chlorine (enhanced parallel ion signal) but not in the case of iodine. This result is in
As has been shown in this section, there has been considerable disagreement over
laser-induced reorientation over the past decade. However, it is now accepted, in
light of the results of Ellert $et$ $al$ (1998) and Posthumus $et$ $al$ (1998), that I$_2$ is not
reorientated (unlike originally concluded by Dietrich $et$ $al$ 1993). Furthermore,
Posthumus $et$ $al$ (1998) has shown that unaligned molecules are ionized (see figure
1.31), again contrary to the observations of Strickland $et$ $al$ 1992. In the case of
lighter molecules such as N$_2$ and Cl$_2$, reorientation is now accepted, but hasn't been
quantified completely.
From the point of view of the present work, the technique suggested by Ellert $et$ $al$
(1998) is preferable to that of Posthumus $et$ $al$ (1998), it is less time-consuming, both
in laser time and computation time. As a consequence, this technique is used as a
starting point for the experimental investigation into laser-induced reorientation in
carbon dioxide (chapter 5).

1.5.2 Laser-induced reorientation - theoretical results
Following the experiments of Normand $et$ $al$ (1992), Friedrich and Herschbach
(1995) addressed the problem of intense laser-induced molecular reorientation from
a theoretical standpoint. The authors proposed a mechanism for reorientation of
molecules involving the interaction of the electric field vector of the laser radiation
with the anisotropic molecular polarizability. Friedrich and Herschbach (1995)
suggested that the laser field creates an induced dipole moment in the molecules, which generates pendular eigenstates. The motion of the molecule is therefore modified: rather than just rotating, the molecule oscillates back and forth around the laser polarization direction.

Consider a linear molecule, treated as a rigid rotor, with a permanent dipole $\mu$ along the internuclear axis, and polarizability components $\alpha_\perp$ and $\alpha_\parallel$ perpendicular and parallel to the axis. If this molecule is subjected to a time varying electric field given by:

$$E = E_0 f(t) \cos(\omega t)$$

where $f(t)$ is the pulse envelope, $E_0$ is the pulse amplitude and $\omega$ is the frequency of the field, the interaction potentials between the molecule and the field are given by:

$$V_\mu(\theta) = -\mu E \cos \theta$$

$$V_\alpha = -\frac{1}{2} E^2 \left[ (\alpha_\parallel - \alpha_\perp) \cos^2 \theta + \alpha_\perp \right]$$

where $V_\mu$ is the potential created by the interaction of the field with the permanent moment, and $V_\alpha$ is the potential created by the induced moment. $\theta$ is the angle between the molecular axis and the electric field direction. For a molecule with $\alpha_\perp < \alpha_\parallel$ the interaction of the induced moment with the field will create potential minima at $\theta = 0^\circ$ and $\theta = 180^\circ$, forcing the molecule into alignment with the laser field. The degree of alignment for a molecule is quantified by the expectation value of $\cos^2 \theta$, $\langle \cos^2 \theta \rangle$. If the molecule is perfectly aligned, $\langle \cos^2 \theta \rangle = 1$, whereas if the molecules are isotropic, $\langle \cos^2 \theta \rangle = 1/3$.

The interaction of the induced moment with the electric field creates pendular states, where the molecular axis is trapped by the electric field. Importantly, the evolution of these states depends strongly on the laser pulse intensity profile. In the case of picosecond pulses, the molecule is able to adiabatically adjust to the electric field, and forms stable pendular states. However, in the case of femtosecond pulses, the molecule does not have time to form pendular states, and is rapidly rotated by the field.

1.6 Coulomb explosion and geometry modification of polyatomic molecules

Following the considerable interest in diatomic molecules, beginning with the work of Codling and Frasinski (1987), experimental studies investigating laser-induced
processes in matter progressed to triatomic molecules in 1989 (Frasinski et al. 1989). To date, this has been a rich seam of physical development, not only from the point of view of discovering new phenomena, such as laser-induced bond-angle modification, but also in the development and application of new and exciting experimental techniques. The following sections will deal first with the experimental observations of a number of groups, followed by a brief introduction into the theoretical treatments necessary to continue these studies.

### 1.6.1 Coulomb explosion and geometry modification of polyatomic molecules - experimental techniques: covariance mapping

As the understanding of the behaviour of diatomic molecules developed, experimental and theoretical studies expanded to include small polyatomic molecules. The earliest study (Frasinski et al. 1989) used covariance mapping to identify the ionization channels. Following a discussion concerning the application of the covariance technique to carbon dioxide, covariance maps of N$_2$O and SO$_2$ were presented. It was observed that, within a 600 fs, 600 nm laser pulse, focused to $3 \times 10^{16}$ W/cm$^2$, N$_2$O retains its linear structure. The end nitrogen and oxygen are released in opposite directions along the laser polarization with considerable momentum, and the middle nitrogen is released with a small amount of momentum in the direction of the end nitrogen. This was indicated by the middle ion being correlated with the end ions. In the case of the bent SO$_2$ molecule, these correlations are observed to be far broader, hence the sulphur ion carries a more considerable amount of momentum from the reaction.

Luk et al. 1992 performed an elegant experiment on N$_2$O to determine how the molecule was dissociatively ionizing in the laser field. They used high purity $^{14}$N$^{15}$N$^{16}$O, and subjected it to a 600 fs 248 nm KrF* laser pulse, focused to $3 \times 10^{16}$ W/cm$^2$. Following fragmentation, $^{15}$N ions from the centre of the molecule were detected with much lower kinetic energy than either of the end ions. Furthermore, it was found that atoms at the end of the molecule were more easily ionized than that in the centre. A comparison was made to fragmentation patterns observed with high-energy ion impact fragmentation. It was suggested that this effect may be due to laser-induced reorientation of the molecule.

The first detailed studies of the laser-induced Coulomb explosion of a triatomic were
carried out in 1994 by Frasinski et al (1994) and Cornaggia et al (1994) both of whom employed titanium:sapphire laser systems to generate short laser pulses which initiated energetic Coulomb explosion in carbon dioxide. The laser parameters for these two experiments are summarised in table 1.4.

<table>
<thead>
<tr>
<th>Publication</th>
<th>Wavelength (nm)</th>
<th>Pulse length (fs)</th>
<th>Focused intensity (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frasinski et al 1994</td>
<td>794</td>
<td>200</td>
<td>$10^{16}$</td>
</tr>
<tr>
<td>Cornaggia et al 1994</td>
<td>790</td>
<td>150</td>
<td>$5 \times 10^{15}$</td>
</tr>
</tbody>
</table>

Frasinski et al 1994 continued the previous studies on N₂O and SO₂. At the time of writing this publication, the question of laser-induced reorientation had not been resolved, hence Frasinski et al (1994) referred to the work of Normand et al (1992) and Dietrich et al (1993). In Frasinski et al 1994, a two-dimensional covariance map was recorded for CO₂. The results from this experiment are shown in figure 1.35(a).

The first observation made from this map was that the major fragmentation channel was the (2,2,2) channel, there the numbers in parenthesis represent the charge of the ions, hence $\text{CO}_2^{2+} \rightarrow \text{O}^{M+} + \text{C}^{N+} + \text{O}^{P+}$ where $M+N+P=Z$. Frasinski et al (1994) also performed a simulation of the two-dimensional covariance map, which is shown in figure 1.34(b). As can be seen the major features of figure 1.34(a) are well-reproduced by this simulation.

It was observed that the fragmentation of CO₂ was charge symmetric. This term is somewhat counter-intuitive, in which channels such as the (2,2,1) are referred to as symmetric (in addition to the (1,1,1), (2,2,2) and (3,3,3) channels) whereas the (1,3,1) channel is referred to as asymmetric. The term symmetric implies the difference in charge between any two ions from an exploding molecule differ by no more than one unit of charge. In the two-dimensional covariance experiment of Frasinski et al (1994), no substantially asymmetric channels were observed. Those channels observed are shown in table 1.5, along with the associated kinetic energy release (KER).

As discussed above, Luk et al 1992 observed higher ion yields from the end atoms of N₂O as opposed to the central nitrogen atom, referred to as 'site specific' ionization. In Frasinski et al 1994, no such behaviour was observed in the case of CO₂. However, the experiment of Luk et al (1992) was performed with very short wavelength laser pulses, hence it may be unfair to make a comparison.
Figure 1.34. (a) Two-dimensional covariance map of CO\textsubscript{2} recorded at 794 nm at an intensity of 10\textsuperscript{16} W/cm\textsuperscript{2}. (b) Simulation of the two-body and charge symmetric three-body channels. (From Frasinski et al. 1994)

Table 1.5. Fragmentation channels from Frasinski et al. (1994).

<table>
<thead>
<tr>
<th>Channel</th>
<th>KER (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,1)</td>
<td>6</td>
</tr>
<tr>
<td>(1,1,1)</td>
<td>17</td>
</tr>
<tr>
<td>(1,2,2)</td>
<td>33</td>
</tr>
<tr>
<td>(2,1,2)</td>
<td>42</td>
</tr>
<tr>
<td>(2,2,2)</td>
<td>66</td>
</tr>
<tr>
<td>(2,2,3)</td>
<td>81</td>
</tr>
<tr>
<td>(3,3,3)</td>
<td>110</td>
</tr>
</tbody>
</table>
Cornaggia et al 1994 recorded two- and three-dimensional maps of carbon dioxide (see table 1.4 for laser conditions). The fragmentation channels observed in the three-dimensional correlation map are shown in table 1.6, along with the associated kinetic energy release. As with Frasinski et al 1994, the kinetic energy release associated with the Coulomb explosion of CO$_2$ was found to be around 50% less than expected from the ground state internuclear separation.

Interestingly, Cornaggia et al 1994 reported two extra high-energy channels from CO$_2$ as compared to Frasinski et al (1994), namely the (2,3,2) and (2,3,3) channels. As the laser conditions are similar, it seems more likely that this is a consequence either of the data processing technique (two-dimensional covariance as opposed to three-dimensional correlation coefficient) or experimental differences. The observation of the (2,3,2) channel in particular is important, as this observation showed that the central atom of a triatomic molecule might be more heavily ionized than the terminal atoms. As discussed above, Frasinski et al (1994) reported that this process was not observed in carbon dioxide.

Even so, the overall observation of these two experiments was that CO$_2$ Coulomb explodes from around double the internuclear separation. A comparison between the results of both publications is shown in table 1.7, along with kinetic energy release.

### Table 1.6. Fragmentation channels from Cornaggia et al (1994).

<table>
<thead>
<tr>
<th>Channel</th>
<th>KER (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2,2,2)</td>
<td>62</td>
</tr>
<tr>
<td>(2,3,2)</td>
<td>87</td>
</tr>
<tr>
<td>(2,2,3)</td>
<td>92</td>
</tr>
<tr>
<td>(2,3,3)</td>
<td>100</td>
</tr>
<tr>
<td>(3,3,3)</td>
<td>130</td>
</tr>
</tbody>
</table>

### Table 1.7. Total KER for the Coulomb explosion of carbon dioxide as reported by Frasinski et al and Cornaggia et al, both 1994. The Coulombic kinetic energy release (CKE) is also shown, along with the ratio $k = \frac{\text{KER}}{\text{CKE}}$.

<table>
<thead>
<tr>
<th>Channel</th>
<th>CKE (eV)</th>
<th>Frasinski et al 1994</th>
<th>Cornaggia et al 1994</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,1,1)</td>
<td>31</td>
<td>17</td>
<td>0.55</td>
</tr>
<tr>
<td>(1,2,2)</td>
<td>87</td>
<td>33</td>
<td>0.38</td>
</tr>
<tr>
<td>(2,1,2)</td>
<td>74</td>
<td>42</td>
<td>0.57</td>
</tr>
<tr>
<td>(2,2,2)</td>
<td>124</td>
<td>66</td>
<td>0.51</td>
</tr>
<tr>
<td>(2,2,3)</td>
<td>161</td>
<td>81</td>
<td>0.57</td>
</tr>
<tr>
<td>(2,3,2)</td>
<td>174</td>
<td>87</td>
<td>0.50</td>
</tr>
<tr>
<td>(2,3,3)</td>
<td>223</td>
<td>100</td>
<td>0.45</td>
</tr>
<tr>
<td>(3,3,3)</td>
<td>279</td>
<td>110</td>
<td>0.39</td>
</tr>
</tbody>
</table>
(KER) and the Coulombic kinetic energy release (CKE), which is the kinetic energy expected if the Coulomb explosion from the internuclear separation. The ratio \( k = \frac{\text{KER}}{\text{CKE}} \) is also shown.

In analysing their two- and three-dimensional correlation maps, Cornaggia et al (1994) brought up the question of molecular geometry to the present work. Despite a lack of quantitative analysis, this publication raised important question about the assumption that the molecule was static within the laser pulse. Furthermore, Cornaggia et al (1994) proposed that laser-induced reorientation of the molecule may be causing bending.

Investigations into laser-induced nuclear motion were continued by Cornaggia et al (1995a) where acetylene (C\(_2\)H\(_2\)) was subjected to 790 nm 130 fs Ti:S laser pulses in the \(10^{15}-10^{16} \text{ W/cm}^2\) intensity range. Cornaggia et al 1995a chose acetylene as it is linear both as C\(_2\)H\(_2\) and as C\(_2\)H\(_2^+\), hence substantial structural changes were not expected in the first ionization step.

Importantly, this publication recognised the importance of the work of Codling and Frasinski (1993) and Dietrich et al (1993), in that the multiple ionization of molecules was in the field ionization regime (see section 1.1 for discussion). Specifically, Cornaggia et al (1995a) noted that the observed kinetic energies are consistent with Coulomb explosion at double the internuclear separation, and specific reference was made to a 'modified molecular ion'.

Cornaggia et al (1995a) proposed a number of mechanisms for creating this 'modified molecular ion'. Firstly, a simple model was proposed in which molecule stabilises at an extended bond length when the centrifugal force caused by the reorientation equals the binding energy of the molecule. A second, more elaborate postulate was also made which involved bond softening population trapping in vibrationally excited states (Zavriyev et al 1993).

Two-dimensional correlation maps were recorded at \(2.5 \times 10^{15} \text{ W/cm}^2\). The ionization channels were identified by examining the distribution of ion momentum along the lines of maximum correlation. The authors were able to identify the channels by conservation of momentum along the molecular axis. The gradient of the correlation islands indicated that, although the molecule remained on average, linear, there was considerable geometry modification before explosion. It was also found that the following relationship holds: \( \alpha(H) = 0.9\alpha(C) \), where \( \alpha(H) \) and \( \alpha(C) \)
are the angles between the laser polarization and the H-H and C-C axes respectively. This implied that the molecular ion undergoes small damped oscillations around the laser polarization, and that the oscillation of the H atoms was smaller than for the C atoms. Cornaggia et al (1995a) explained this in terms of the moments of inertia of the two axes.

In a further experiment, Cornaggia (1995b) investigated laser-induced nuclear motion in more detail. Two relatively large polyatomic molecules were examined in the femtosecond regime. Allene (C₃H₄) and propane (C₃H₈) were field ionized by 130 fs laser pulses. See figure 1.35 for a simple representation of the structure of each molecule. In each case, the relative abundance of molecular ions was examined. The fragmentation of both molecules was examined from the standpoint of the different types of bonds within the molecules.

![Schematic of the structure of allene and propane](image)

When two-dimensional correlation maps are recorded for allene and propane, the fragmentation mechanism of the carbon chain may be clearly seen. In the case of allene, the correlations occur in well-defined islands, as reproduced in figure 1.36(a). However the carbon ions from propane have a broad, elliptical distribution, which indicates that the structure of the carbon chain is 'blurred', either by deformation or through the pre-dissociation of the molecule.

As the fragmentation process in propane is complex, involving more than one step, Cornaggia (1995b) focused on understanding the dynamics of the Coulomb explosion of the carbon chain in allene. A simulation of the two-dimensional correlation map was performed. Three triangular distributions were used to describe the bond length (r), bend angle (θ) and the alignment with the laser field (ϕ). These co-ordinates are illustrated in figure 1.37 for an arbitrary triatomic molecule. In the case of Cornaggia 1995, the two 'arms' of the molecule are set at the same length.
Once the geometry was established, the final momenta of the ions were calculated by allowing the ions to explode to infinity. The simulated two-dimensional correlation map is reproduced in figure 1.36(b). As can be seen, the agreement between the experimental and simulated results is very good, considering the simplicity of the model. The best fit distributions are given in table 1.8, where $r_c = 2.1 r_e$. In allene, the equilibrium bond length for the carbon chain is $r = 1.308 \text{ Å}$ (Herzberg 1966).

As can be seen, Cornaggia (1995) found it necessary to allow the molecule to explode from double the unperturbed internuclear separation, in agreement with previous results for polyatomic molecules (Frasinski et al 1994, Cornaggia et al 1994, Cornaggia 1995). As shown in table 1.8, the carbon chain within the molecule
undergoes a large bending motion, which is larger than that expected in the neutral field free molecule.

An important consideration that has come to light in the present work is the effect of sequential dissociation. The bonds in the molecules studied in Cornaggia et al 1995a,b will not necessarily expand at the same rate, and hence there may be some scattering between the ions during Coulomb explosion. Specifically, considerable C₂H₂⁺ signal was observed from C₂H₃, whereas very little C₃H₈⁺ was seen from C₃H₈, indicating propane may undergo sequential dissociation. This is supported by the blurring of the covariance map published in Cornaggia (1995b). This is also consistent with the 'scattering' picture, as the carbon backbone is surrounded by hydrogen ions.

Cornaggia 1996 investigated the geometry of the carbon dioxide molecule Coulomb exploding in a 130 fs 790 nm laser pulse focused to 10¹⁵ W/cm². Figure 1.38(a) shows the experimental two-dimensional correlation map, recorded under the laser conditions as described above. Figure 1.38(a) was recorded with the laser polarization direction parallel to the detector axis. Again, the experimental maps were reproduced by the Monte Carlo technique first described in Cornaggia 1995a.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Minimum</th>
<th>Peak</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length (r)</td>
<td>0.5rₑ</td>
<td>rₑ</td>
<td>1.5rₑ</td>
</tr>
<tr>
<td>Bend angle (θ)</td>
<td>140°</td>
<td>180°</td>
<td>220°</td>
</tr>
<tr>
<td>Alignment (ϕ)</td>
<td>-40°</td>
<td>0°</td>
<td>40°</td>
</tr>
</tbody>
</table>
As in the case of the simulations of allene, the molecule was described by three triangular distributions ($r$, $\theta$ and $\phi$, see figure 1.37).

Figure 1.38(b) shows the simulated two-dimensional correlation map of carbon dioxide. Comparing this with figure 1.38(a) (experimental data) the quality of the fit is visually good. The general shape and position of the correlation islands is reproduced, indicating the validity of the distributions found. The best-fit distributions reported by Cornaggia 1996 are shown in table 1.9. As can be seen, the Coulomb explosion occurs from double the internuclear separation. As originally suggested in Cornaggia et al 1994, the results in table 1.9 show that the molecule undergoes large scale bending motions around an average linear geometry. The best fit parameters are listed in the following table.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Minimum</th>
<th>Peak</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length ($r$)</td>
<td>$0.5r_e$</td>
<td>$r_e$</td>
<td>$1.5r_e$</td>
</tr>
<tr>
<td>Bend angle ($\theta$)</td>
<td>$140^\circ$</td>
<td>$180^\circ$</td>
<td>$220^\circ$</td>
</tr>
<tr>
<td>Alignment ($\phi$) for (1,1,1)</td>
<td>$-60^\circ$</td>
<td>$0^\circ$</td>
<td>$60^\circ$</td>
</tr>
<tr>
<td>Alignment ($\phi$) for (1,2,1)</td>
<td>$-40^\circ$</td>
<td>$0^\circ$</td>
<td>$40^\circ$</td>
</tr>
<tr>
<td>Alignment ($\phi$) for (2,2,1)</td>
<td>$-40^\circ$</td>
<td>$0^\circ$</td>
<td>$40^\circ$</td>
</tr>
<tr>
<td>Alignment ($\phi$) for (2,2,2)</td>
<td>$-30^\circ$</td>
<td>$0^\circ$</td>
<td>$30^\circ$</td>
</tr>
</tbody>
</table>
fit distributions are given in terms of \( r_c = 2r_e \). In carbon dioxide, the equilibrium bond length is \( r = 1.16 \) Å (Herzberg 1966).

Cornaggia (1996) suggested that the bending and stretching processes were caused by the interaction of the laser field with the electrons surrounding the molecule. It was suggested that the electronic polarizability will cause the electronic structure to be modified, and the electron-nuclei interaction will allow the molecular structure to be modified. However, this mechanism was not quantified.

In both Cornaggia 1995 and 1996, the author reported that the average straight geometry of the molecules in question (\( \text{C}_3\text{H}_4 \) and \( \text{CO}_2 \) respectively) was unchanged, but large bending motions were induced by the laser field. Furthermore, Cornaggia (1996) hinted that the laser-induced Coulomb explosion of a triatomic molecule may involve reorientation, as previously seen in diatomic molecules (see section 1.5). The author continued his investigations of nuclear motion on small molecules by investigating the Coulomb explosion of \( \text{SO}_2 \).

Using laser pulses 50 fs in duration, with a wavelength of 790 nm, Cornaggia et al (1996) induced Coulomb explosion of \( \text{SO}_2 \) with field intensities of \( 3 \times 10^{15} \) Wcm\(^{-2} \).

In this publication, direct reference was made to the interplay between the permanent and induced dipole moments. Cornaggia et al (1996) pointed out that the permanent dipole moment of the \( \text{SO}_2 \) molecule lies perpendicular to the O-O axis, hence if laser-induced reorientation involving the permanent dipole was present, there should be a maximum in the oxygen signal perpendicular to the laser polarization direction. However, the oxygen ion signal was found to be at a maximum when the polarization direction was parallel to the detector axis, hence the authors deduced that the molecule was being reoriented by the laser field through its interaction with the induced dipole moment. Cornaggia et al (1996) compared the \( \text{C}^+/\text{O}^+ \) correlations from \( \text{CO}_2 \) with the \( \text{S}^+/\text{O}^+ \) correlations from \( \text{SO}_2 \). These results are shown in figure 1.39(a) and (b) respectively.

Cornaggia et al (1996) observed that the \( \text{C}^+/\text{O}^+ \) correlation from the 'linear' \( \text{CO}_2 \) molecule exhibited a parallelogram contour, whereas the \( \text{S}^+/\text{O}^+ \) correlation from the bent \( \text{SO}_2 \) molecule was elliptical. The authors concluded that the low-order Coulomb channels were from around the bent geometry, where \( \theta \approx 120^\circ \). However, when Cornaggia et al (1996) examined the \( \text{S}^{3+}/\text{O}^{2+} \) correlation, as shown in figure 1.40, they found a pronounced parallelogram shape, hence Coulomb explosion was
occurring from a linear geometry, where $\theta \approx 180^\circ$. This observation lead to the conclusion that the evolution of the molecular geometry depended on the ionization channel. However, this evolution between low and high ionization channels was not explained by the electron configuration of the molecular ions. Cornaggia et al 1996 expected the highest channels to originate from bent molecule, however, explosion from a linear configuration was observed.

The correlation map experiments of Cornaggia and co-workers have given important insights into the interaction of an intense laser field and small polyatomic molecules.
1.6.2 Coulomb explosion and geometry modification of polyatomic molecules - experimental techniques: momentum imaging

A new experimental technique was introduced in 1998 that addressed the question of molecular geometry determination. Yamanouchi and co-workers introduced the mass-resolved momentum imaging (MRMI) technique, which uses a high-resolution TOFMS to measure the momentum of ions emitted following Coulomb explosion as a function of laser polarization direction. The polarization direction is rotated in 6-degree intervals and a 100 shot TOF spectrum recorded at each polarization setting. The ion signal for each ion species is then displayed in polar form, either as a two-dimensional contour plot or as a three-dimensional surface plot. The ion momentum is plotted radially, and the polar co-ordinate represents the polarization direction. By analysing these MRMI maps, it becomes possible to extract the geometrical structure of the molecule just before Coulomb explosion. Yamanouchi and co-workers have performed experiments on a number of di- and triatomic molecules.

In the case of diatomic molecules, Hishikawa et al (1998) used the MRMI technique to examine the Coulomb explosion of N₂. The authors were able to identify the Coulomb explosion channels in N₂ as shown in table 1.10. When the kinetic energy release is converted to internuclear separation through equation 1.9, it can be seen that the molecule Coulomb explodes at around the same internuclear separation
(around 2.2 Å) as compared to the field free separation (1.1 Å). This is in qualitative agreement with previous experimental results, in that the Coulomb explosion occurs at around double the ground state separation.

**Table 1.10.** Coulomb explosion channels and associated KER for N$_2$ exposed to 100 fs 795 nm laser pulses at $3.5 \times 10^{15}$ W/cm$^2$. The KER is converted to internuclear separation, R using equation 1.* (Hishikawa *et al* 1998)

<table>
<thead>
<tr>
<th>Total charge, Z (a.u.)</th>
<th>(p,q) (a.u.)</th>
<th>KER (eV)</th>
<th>R (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>(1,1)</td>
<td>6.6</td>
<td>2.18</td>
</tr>
<tr>
<td>3</td>
<td>(1,2)</td>
<td>13.6</td>
<td>2.12</td>
</tr>
<tr>
<td>4</td>
<td>(1,3)</td>
<td>22</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td>(2,2)</td>
<td>24.2</td>
<td>2.38</td>
</tr>
<tr>
<td>5</td>
<td>(2,3)</td>
<td>36</td>
<td>2.4</td>
</tr>
<tr>
<td>6</td>
<td>(3,3)</td>
<td>56</td>
<td>2.31</td>
</tr>
</tbody>
</table>

Hishikawa *et al* (1998) also used MRMI to examine the dynamic behaviour of the SO$_2$ molecule during Coulomb explosion. Using a 795 nm 100 fs laser pulses focused to $5.4 \times 10^{15}$ W/cm$^2$, MRMI maps were recorded for SO$_2$ over 360° in 6° intervals. Hishikawa *et al* (1998) first examined the MRMI maps of the O$^+$ / S$^{2+}$ ions, and noted the maximum of the ion signal lay parallel to the laser polarization direction (i.e. when the polarization direction was parallel to the detector axis). Following the results of Cornaggia *et al* 1996, this behaviour was assigned to the oxygen ions rather than the sulphur ions, indicating the O-O axis of the molecule was strongly aligned with the laser electric field. The MRMI map of O$^+$ / S$^{2+}$ is presented in figure 1.41(a). Hishikawa *et al* (1998) then examined the MRMI maps of SO$^+$ and SO$^{2+}$, which indicated that the two-body fragmentation channels SO$^+$ + O$^+$ and SO$^{2+}$ + O$^+$ were present. The MRMI map of SO$^{2+}$ is presented in figure 1.41(b).

![Figure 1.41. MRMI maps of SO$_2$ at 5.4 $\times$ 10$^{15}$ W/cm$^2$. (a) O$^+$ / S$^{2+}$ ions, (b) SO$^{2+}$ ions and (c) S$^{3+}$ ions. In all cases, 100 fs 795 nm laser pulses have been used. (Adapted from Hishikawa *et al* 1998)](image-url)
Hishikawa et al (1998) reported that two-body channels were found to be minor as compared to three-body channels, which was evident from the TOF spectrum being dominated by atomic ions, indicating full Coulomb explosion of the SO$_2$ molecule. As Hishikawa et al (1998) found, the charge-to-mass degeneracy of the O$^+$ / S$^{2+}$ (m/q = 16 au) and O$^{2+}$ / S$^{4+}$ (m/q = 8 au) complicates identifying the fragmentation dynamics of the molecule. However, the authors got round this problem by examining the MRMI map of the S$^{3+}$ ion (m/q = 32/3 au), which clearly cannot be degenerate with an oxygen ion.

The shape of the S$^{3+}$ MRMI map, presented in figure 1.41(c) is markedly different from the O$^+$ / S$^{2+}$ and SO$^{2+}$ maps (figure 1.41(a) and (b) respectively). The maximum of the S$^{3+}$ signal is perpendicular to the laser polarization direction, indicating that the ions originate from aligned molecules with a bent geometry. This process is illustrated in figure 1.42 for a linear and bent triatomic AB$_2$, field ionized to AB$_2$$^+$.

**Figure 1.42.** Comparison of the Coulomb explosion of a linear and bent triatomic AB$_2$. In the case of the linear molecule, the A$^{2+}$ ions are emitted directly along the laser polarisation (ε), and the B$^{3+}$ ions have zero momentum, resulting in the MRMI map of the S$^{3+}$ ion being maximum at zero. In the case of the bent geometry, the A$^{2+}$ ions are emitted around the laser polarization, and the B$^{3+}$ ions are emitted perpendicular to the polarization with non-zero momentum, as shown bottom right.

Hishikawa et al (1998) quantified the geometry of the SO$_2$ molecule by assuming symmetric channels dominated the explosion. They approximated the critical bend angle $\gamma_c$ (which shall be referred to as $\theta_c$ to be consistent with figure 1.37 using the following relationship:

![](image.png)
\[ \theta_c = 2 \tan^{-1}\left( \frac{2p(O^{q+})}{p(S^{3+})} \right) \]  

Equation 1.17

where \( p(O^{q+}) \) represents the component of the momentum of the \( O^{q+} \) ion parallel to the polarization direction, \( q = 1, 2 \) au, and \( p(S^{3+}) \) is the total momentum of the \( S^{3+} \) ion. They found \( p(O^+) = 170 \times 10^3 \) amu ms\(^{-1} \), \( p(O^{2+}) = 257 \times 10^3 \) amu ms\(^{-1} \) and \( p(S^{3+}) = 240 \times 10^3 \) amu ms\(^{-1} \). Applying equation 1.17 to these momenta gave \( \theta_c = 110^\circ \) for the \( (1,3,1) \) channel, and \( \theta_c = 130^\circ \) for the \( (2,3,2) \) channel. Hence, in the case of \( \text{SO}_2^{5+} \) and \( \text{SO}_2^{7+} \), Hishikawa \textit{et al} (1998) observed that the bent structure of the \( \text{SO}_2 \) molecule was retained during Coulomb explosion. This was concluded as \( \theta_c \) for the \( (1,3,1) \) and \( (2,3,2) \) channels was not found to be significantly different from \( \theta_e = 119.5^\circ \), where \( \theta_e \) is the equilibrium bend angle.

Using a variation of equation 1.8, Hishikawa \textit{et al} (1998) calculated the critical bond length \( r_c(O-S) \) in Å using the following expression:

\[ r_c(O-S) = \frac{204.6}{E_{\text{total}}} \]  

Equation 1.18

where \( E_{\text{total}} \) is the total kinetic energy release in eV. Hishikawa \textit{et al} (1998) found \( r_c = 2.5 \) Å and 3.3 Å for the \( (1,3,1) \) and \( (2,3,2) \) channels respectively, which is in general agreement with other experimental results (see section 1.4.1). However, the bend angle measurements of Hishikawa \textit{et al} (1998) shed doubt on the results of Cornaggia \textit{et al} 1996. The differences between the conclusions of these experiments may be an instrumental effect, such as the ineffective collection of ions with orthogonal trajectories.

The MRMI technique was used by Hishikawa \textit{et al} (1999a) to investigate the geometry of carbon dioxide. As in Hishikawa \textit{et al} (1998), 100 fs, 795 nm laser pulses were used. In the \( \text{CO}_2 \) experiment, a focused laser intensity of \( 1.1 \times 10^{15} \) Wcm\(^{-2} \) was used (as compared to \( 5.4 \times 10^{15} \) Wcm\(^{-2} \) in the \( \text{SO}_2 \) experiment). Hishikawa \textit{et al} (1999a) recorded MRMI maps for the atomic fragments following Coulomb explosion. Figure 1.44. shows the \( O^{p+} (p = 1-3) \) ions (left-hand side) and the \( C^{q+} (q = 1-3) \) ions (right-hand side). The authors made two observations based on these results. Firstly, the oxygen ions are emitted along the laser polarization, in agreement with the observations of Cornaggia \textit{et al} (1994), Frasinski \textit{et al} (1994) and
Figure 1.43. MRMI maps of the $O^\pi (p = 1 - 3)$ and $C^\pi (q = 1 - 3)$ produced from the Coulomb explosion of CO$_2$. The three points on the $C^\pi (q = 1 - 3)$ indicate the momentum generated by bends of 180°, 165° and 150°. (Adapted from Hishikawa et al. 1999a)

Cornaggia (1996). No comment was made as to whether the molecules were being reorientated by the laser field, just that the ions originated from molecules aligned with the laser field.

Secondly, the carbon ion signal was observed to peak at zero momentum, implying a linear geometry, as shown in figure 1.42. Using the approximation made in Hishikawa et al. (1998), as shown in equation 1.17, three carbon ion momenta were converted to bend angle for the most abundant symmetric fragmentation channels. These points are shown in figure 1.43, and illustrate that substantial bending motion is induced by the laser field. Considering that the mean amplitude of bending is 12.5° for the ground state vibrational level of neutral CO$_2$, the fact that bends of up to 30° can be supported shows the strength of this induced motion.

To quantify the induced nuclear motion, Hishikawa et al. 1999a performed a trial-and-error simulation of the MRMI maps as shown in figure 1.44. To allow a
Figure 1.44. Simulated MRMI maps of the \( \text{O}^{q^+} \) (\( p = 1 - 3 \)) and \( \text{C}^{q^+} \) (\( q = 1 - 3 \)) produced from the Coulomb explosion of \( \text{CO}_2 \). Compare with figure 1.4. (Adapted from Hishikawa et al 1999a)

A legitimate comparison to be made with the experimental results, all possible fragmentation channels must be taken into account. The simulation process was performed as follows:

(i) Bond lengths, bend angles and alignment angles were chosen for each explosion channel and the momentum generated was calculated.

(ii) MRMI maps were generated for each of the atomic ion species by summing contributions from each channel weighted according to the relative abundance of the relevant \( \text{O}^{p^+} \) fragment.

(iii) A comparison was made between the simulated and experimental results.

Steps (i) to (iii) were repeated until a best fit was found.

Clearly, summing single values for the bond length and bend angle is unphysical, hence a distribution was assigned to each parameter. The bond length distribution \( F(r) \) was chosen to be:
\[ F(r) \propto \exp \left[ -a \left( \frac{1}{\sqrt{r}} - \frac{1}{\sqrt{r_{\text{peak}}}} \right)^2 \right] \]

where \( r_{\text{peak}} \) is an adjustable parameter and \( a \) is chosen to give a FWHM of 1 Å in agreement with calculations based on the \( \text{O}^{n+} \) fragments. The bend angle distribution was chosen to be:

\[ F(\theta) \propto \exp \left[ -\left( \frac{\theta - \pi}{\theta_{\text{wid}} / 2\sqrt{2\ln 2}} \right)^2 \right] \]

again, where \( \theta_{\text{wid}} \) is adjustable. Hishikawa et al (1999a) used the alignment distribution derived by Friedrich and Herschbach (1995), as shown below:

\[ F(\phi) \propto \exp \left[ -\frac{\sin^2 \phi}{2\phi_{\text{wid}}^2} \right] \]

where \( \phi_{\text{wid}} \) is the adjustable parameter.

After a number of iterations, the best fit MRMI maps were generated. These are reproduced in figure 1.44. When these simulated maps are compared with the experimental maps, there is a good agreement. The variation of parameters \( r_{\text{peak}} \) and \( \theta_{\text{wid}} \) with total charge \( Z \) is shown in table 1.11. As can be seen, there is a gradual increase of \( r_{\text{peak}} \) with \( Z \). Hishikawa et al 1999 cite this behaviour as being consistent with the enhanced ionization model of Posthumus et al (1996), where each successive ionization step occurs as the internuclear separation increases (see section 1.4). 

<table>
<thead>
<tr>
<th>( Z )</th>
<th>( r ) (Å)</th>
<th>( \theta_{\text{wid}} ) (deg)</th>
<th>( \phi_{\text{wid}} ) (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.62</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.68</td>
<td>43</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>1.68</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.74</td>
<td>35</td>
<td>31</td>
</tr>
<tr>
<td>7</td>
<td>1.86</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2.09</td>
<td>28</td>
<td>24</td>
</tr>
<tr>
<td>9</td>
<td>2.44</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

As is also apparent from table 1.11, the lower charge states exhibit large-scale bending motion. As can be seen in table 1.11, there is a systematic decrease in the width of the bend distribution with increasing \( Z \). Hishikawa et al (1999a) pointed out that light-dressed potential energy surfaces (LDPES) would be created, analogous to
the H₂ case (Zavreyiev et al. 1993). This decrease in the width of the bend angle distribution is attributed to population transfer from the linear ground state to bent excited states. This coupling occurs in the $10^{12} - 10^{14} \text{ Wcm}^{-2}$ intensity range, hence will be generated in the leading edge of the laser pulse used in this work. As this behaviour is intensity dependant, the higher fragmentation channels, generated in regions of high peak intensity, would have less time to evolve into the excited states, hence the bend distribution would be less affected.

1.6.2 Coulomb explosion and geometry modification of polyatomic molecules - theoretical discussion

Hishikawa and co-workers discussed their experimental observations in terms of light-dressed potential energy surfaces (LDPES). This treatment is analogous to that discussed for dissociative processes in diatomic molecules in section 1.3, where Zavriyev et al. (1990, 1993), Giusti-Suzor et al. (1995) and references therein examined dissociation in terms of light-dressed potentials and adiabatic avoided crossings. Hishikawa and co-workers took a similar approach when examining laser-induced geometry modification and Coulomb explosion in triatomics. In their initial publications (Hishikawa et al. 1998), rather than illustrating the dressing process, the authors discussed excited states that may be accesses through the absorption of one or more photons. Given the complexity of the systems in question, these discussions have been rather simplistic and require a full theoretical treatment. However, molecular bending motions may be explained by dressing the two lowest potential surfaces for the bending motion by the photon energy, as shown in Hishikawa et al. (1999). Here, the bending motion of the CO₂ was explained in terms of LDPES, as the adiabatic avoided crossings allowed the bending motion of the molecule to access geometries unsupported by the ground-state field-free molecule.
Chapter 2. Experimental

2.1 Introduction
This chapter will detail the experimental apparatus employed in the present work. Firstly, a description will be given of the time-of-flight mass spectrometer central to all of the experiments including descriptions and diagrams of the elements of the vacuum system. Secondly, the laser systems that have been used will be detailed, along with the techniques used to generate and amplify the ultra-fast pulses. Thirdly, each of the data collection techniques will be described.

2.2 Experimental apparatus
The three major sections of the experimental apparatus are discussed in the following sections. Firstly, the ultra-high vacuum system is described, followed by the time-of-flight mass spectrometer. Finally, the target gas handling system is discussed.

2.2.1 Ultra-high vacuum system
Figure 2.1 is a schematic of the ultra-high vacuum (UHV) system that houses the time-of-flight mass spectrometer (TOFMS). The vacuum system is based on a modified four-way UHV crosspiece. The flanges on the four major ports are standard 200 mm conflat fittings. Two 70 mm conflat ports have been added mutually perpendicular to the two original axes of the crosspiece to provide the entrance and exit for the laser pulses.

The vacuum system is pumped by a Pfeiffer-Balzers TPU-450H turbomolecular pump with a pumping speed of 450 l/s (N$_2$). This is attached to the base 200 mm conflat flange of the UHV chamber. The turbopump is coupled to a Pfeiffer-Balzers MD-4T oil-free diaphragm pump, with a pumping speed of 3.3 m$^3$/h. The operation of both pumps is governed by a Pfeiffer-Balzers TCP-380 control unit. All UHV seals are standard copper gaskets.

The TOFMS is mounted on the upper conflat flange, which has three 70 mm conflat ports equally spaced on a PCD of 43 mm. Two of these ports are used to mount 11-pin UHV electrical feed-throughs (FT on figure 2.1). A Vacuum Generators MD6 UHV needle valve (NV) is mounted on the remaining port, through which the target gas is introduced.

Two 200 mm conflat flanges are used to seal the side ports of the chamber. One
flange is a standard non-rotatable blank, and the second has three 70 mm conflat ports on a PCD of 86 mm. One of the 70 mm fittings is used to mount a Vacuum Generators VIG-22 ionization gauge (IG on figure 2.1), which is connected to a Vacuum Generators IGC-27 ionization gauge controller. Another of the 70 mm fittings is used to mount an UHV extension piece 10 cm in length, into which is mounted a Spectra LM2 residual gas analyzer (RGA), which consists of a quadrupole mass spectrometer attached to a UHV feed-through. On the atmosphere side of this feed-through is a Spectra LM-10 RF head, interfaced to a Spectra LM-46 Satellite control unit. The Satellite unit is connected to a laboratory PC via an RS-232 cable, and is computer controlled under Microsoft Windows 95. The RGA is used to measure the partial pressures of atoms and molecules with masses from 1 to 100 amu, hence the amount of target gas can be monitored, along with allowing identification of any impurities in the vacuum chamber.
When pumping the vacuum system from atmospheric pressure, the turbo-pump normally accelerates to an operating speed of around 715 Hz within 6 minutes, at which point the ionization gauge can be activated. The point at which the turbopump reaches operating speed is indicated by a drop in the drive current applied to the motor in the pump. During the acceleration stage, 7 A is applied to motor, but above 700 Hz, only 1.5 A is required to maintain the rotation speed. At this time, the pressure is approximately $1 \times 10^5$ mbar, and improves to around $5 \times 10^6$ mbar after 30 minutes. Following baking at 150°C for 24 hours, the vacuum system reaches a typical pressure of $4 \times 10^{-9}$ mbar, which gradually improves over 2-3 days to an ultimate background pressure of $2 \times 10^{-10}$ mbar.

When measuring the pressure in the vacuum chamber, there is a discrepancy between the values indicated by the ionization gauge and the RGA. For pressures between $1 \times 10^{-6}$ mbar and around $1 \times 10^{-9}$ mbar, the RGA and ionization gauge agree. However, the RGA cannot accurately measure pressures below $1 \times 10^{-9}$ mbar.

The following parts have been used in the construction of the TOFMS. All fittings are standard parts, except the four-way cross, which has been modified as shown in figure 2.1, by welding the fixed bore flanges so as to be perpendicular to the two axis of the cross piece. The following parts are manufactured by Vacuum Generators (UK). Stainless steel (S/S) four-way cross with 200 mm conflat ports: ZBX415RI. S/S 200 mm blank conflat flanges ($\times$3): ZFCL8. S/S 70 mm fixed bore flanges ($\times$2): ZFCL45. S/S 70 mm conflat 11-pin electrical feed-through ($\times$2): ZEFT16NW. The following part is manufactured by Cabum-MDC (UK). 70 mm conflat fused-silica viewports ($\times$2): 9722205.

2.2.2 Time-of-flight mass spectrometer

In order to study laser-molecule interactions, it is necessary to identify the ions generated and measure their kinetic energy and momentum. Figure 2.2 is a schematic of the time-of-flight mass spectrometer (TOFMS), which employs the Wiley-McLaren (1955) geometry. This geometry ensures that the total flight time of a particular ion is independent of the point of generation within the laser focus. The main elements of the spectrometer are two extraction grids, referred to as the 'top' and 'bottom' plates. The grids used are tungsten, with an optical transparency of over 95%. Both are situated 1 cm from the laser focus, hence the top-bottom plate
Figure 2.2. Schematic of the time-of-flight mass spectrometer (not to scale).

Application of DC potentials to these grids extracts the product ions from the laser focus. On passing through the top grid, the ions are then accelerated by a potential applied to an 'acceleration-grid', situated 0.53 cm from the top-plate. Attached to the acceleration grid is a 2.5 cm diameter drift-tube, 11 cm in length, which is at the same potential as the acceleration grid, hence the ions then drift through a 'field-free' region.

Figure 2.3 shows a photograph of the TOFMS, inverted on the mounting flange. The detector housing, extraction and acceleration plates and drift tube are all visible.

The force (and hence the acceleration) experienced by ions of different charge-to-mass ratio depends on the electric field along the flight path between the source region and the detector. Hence, there is a temporal separation of the ions along the flight-path according to their charge-to-mass ratio.

A typical set of potentials for the TOFMS is shown in table 2.1. The numbers in
parenthesis correspond to the labeled elements of the detector in figure 2.2. The potentials applied to the top- and bottom-plates and drift-tube (and hence the acceleration grid) have been chosen such that ions produced ±2 mm of the plane equidistant to the top- and bottom-plates will arrive at the detector at the same time. Hence, within this region, the ion flight time is independent of the position at which the ion is produced. These potentials were found by simulating the passage of a number of different charge-to-mass ratios through the spectrometer (for simulation program, see Thomas 1999, appendix 3). This set of potentials was found to be best suited to observing the Coulomb explosion of triatomic molecules, as they allow sufficient resolution of the mass and momentum of the ions produced. For much lighter molecules such as H₂ with consequently lower momentum, the potentials applied to the top- and bottom-plates and the drift tube are lowered dramatically, but maintaining the same ratios. Typically, for molecular hydrogen, a top-plate potential of −5 V is used.

Electrostatic potentials are applied to the top- and bottom-plates and the drift-tube
Table 2.1. Typical potentials applied to the elements within the TOFMS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collector (5)</td>
<td>0 V</td>
</tr>
<tr>
<td>Top face of MCP 2 (4)</td>
<td>-200 V</td>
</tr>
<tr>
<td>Mid-plate washer (3)</td>
<td>-1.4 kV</td>
</tr>
<tr>
<td>Bottom face of MCP 1 (2)</td>
<td>-2.6 kV</td>
</tr>
<tr>
<td>Collection grid (1)</td>
<td>-2.8 kV</td>
</tr>
<tr>
<td>Acceleration grid</td>
<td>-1002 V</td>
</tr>
<tr>
<td>Top plate</td>
<td>-300 V</td>
</tr>
<tr>
<td>Bottom plate</td>
<td>+300 V</td>
</tr>
</tbody>
</table>

through PTFE insulated UHV wire, with each of the three elements attached to a pin on the vacuum side of the electrical feed-through on the top flange (see figure 2.1). The atmosphere side is similarly straightforward: each of the pins is connected directly to a high-voltage connector (PET 2000), connected to a high-voltage supply. At the end of the drift-tube is the ion detector. A detailed schematic of the ion detector is shown in appendix 1. This consists of a pair of Philips Photonics G25-25DT/13 double-thickness resistance-matched micro-channel plates (MCP), 25 cm in diameter mounted in chevron formation. Below the MCPs is an electrostatic grid, which accelerates the product ions from the potential at the end of the drift-tube to 2.8 keV. This causes electrons emitted from the front face of the channel-plates to be turned around, to increase efficiency. This grid is referred to as the 'collection grid'. A potential divider is used to apply the potentials to MCP1 and MCP2 and the collection grid: the relevant circuit is shown in appendix 1, figure A1.1, where the values of all resistors are given in ohms. The bottom of the divider is attached to a high-voltage supply (via a PET 2000 connector), which supplies the potential for the collection grid (point 1 on figures 2.2 and A1.1).

The pair of channel plates have gain of $\sim 10^6$ with an applied voltage across each MCP of 1.2 kV. For positive ions with a kinetic energy of 2.6 keV (the potential at the front of MCP1), the efficiency is 0.5 counts per particle. Three copper washers in contact with the faces of the MCPs are used to apply the potentials, which are picked off at various points along the potential divider. The three washers are indicated as points 2, 3 and 4 on figures 2.2 and A1.1. Electrons leaving the top face of MCP2 strike a copper anode (connection 5): this electron flux is directly proportional to the number of ions arriving at the front face of MCP1. The ion signal is then generated by allowing the electron current to go earth through a 1 MΩ resistor, and measuring
the potential difference generated with respect to earth.

To adjust the temporal width of the output channel-plate pulses, a 47Ω variable resistor is used in series with a 10 nF capacitor. Without this RC circuit to shape the channel-plate output, the pulse length is typically 10-15 ns, whereas with the RC circuit, the pulses can be stretched to 50 ns. This allows the DSO to record the detector output at a lower sample rate. To improve the angular resolution of the detector, a removable aperture can replace the collection grid directly below the MCPs. The aperture consists of a 22 mm diameter copper disk with a 3 mm diameter hole in the centre, mounted onto the end of the drift-tube using a stainless steel insert. This is also shown in appendix 1.

2.2.3 Target gas supply

The target gas is introduced into the source region of the TOFMS through a hypodermic needle, situated 1 cm from the laser focus. The needle is equidistant between the top- and bottom-plates, and is perpendicular to the axis of the TOFMS and the path of the laser pulse. The connection between the hypodermic needle and the input valve (NV on figure 2.1) is through a 5 mm diameter PTFE tube. Typically,
when the target gas is introduced into the vacuum system, the background pressure rises from $2 \times 10^{-10}$ mbar to around $1 \times 10^{-7}$ mbar as measured on the ionization gauge (IG). The high-vacuum side of the gas-line is constructed from $\frac{1}{4}''$ stainless steel tubing and Swagelok $\frac{1}{4}''$ fittings and valves. The gas-line is all metal, so the entire gas-line can be baked. Stainless steel is used so toxic or corrosive gases can be handled safely. A schematic of the gas-line is presented in figure 2.4.

The gas-line is pumped to an ultimate background pressure of $1.2 \times 10^{-3}$ mbar by an Edwards RV3 rotary pump, and can be baked using a heating tape. When using a gas target, a lecture bottle of spectroscopic purity gas with regulator are used to fill the gas-line after it has been evacuated to the ultimate pressure ($\sim 1 \times 10^{-3}$ mbar). For liquid targets, a Pyrex ampoule and on-off valve are used. Again, the ampoule is evacuated to remove the air from the liquid, then the on-off value opened. To convert from $\frac{1}{4}''$ stainless steel tubing to 70 mm conflat, a custom fitting is made, using a blank 70 mm flange with a $\frac{1}{4}''$ Swagelok male pipe connector welded into it. This is shown in figure 2.5, and is referred to in figure 2.4.

![Diagram of Swagelok to 70 mm conflat conversion piece](image)

**Figure 2.5.** $\frac{1}{4}''$ Swagelok to 70 mm conflat conversion piece.

2.3 **Femtosecond laser**

In the present work, laser pulses of 60 fs have been used to field-ionize a range of triatomic molecules and atomic gases. The laser system uses chirped-pulse amplification (Strickland and Mourou 1985) of 50 fs pulses from a titanium: sapphire (Ti:S) oscillator.
2.3.1 The 50 femtosecond laser system

Figure 2.6 shows a diagram of the laser system used in the present work. A Spectra Physics BeamLok 171 argon-ion laser pumps a Spectra Physics 3960C Ti:S oscillator, producing a pulse energy of around 10 nJ in a pulse duration, $\tau = 50$ fs at a wavelength of $\lambda = 790$ nm. The oscillator generates these short pulses at a frequency of 82 MHz. It is necessary to use chirped-pulse amplification (CPA) in the case of such short pulses, as it is impossible to generate the pulse energies necessary for these experiments without destroying the pulse quality. An all-reflective stretcher, comprising of two 1500 lines/mm gratings (G1 and G2 on figure 2.6) and a concave mirror (CM) with a radius of curvature (ROC) of 730 mm, is used to increase the pulse duration to 180 ps. The oscillator is isolated from reflections by a Faraday rotator (FI on figure 2.6) that also switches the stretched pulse into the amplifier by rejecting it perpendicular to the oscillator pulse. The stretched pulses are amplified in a multi-pass confocal amplifier containing a Ti:S crystal (Crystal Systems, figure-of-merit = 150 and $\alpha_{514} = 4.8$), pumped with 67 mJ from a Spectra Physics GCR 270-10 Nd: YAG laser, with a pulse length of 8 ns. The stretched pulses pass through the crystal five times, controlled by four spherical mirrors, each with a radius of curvature of 2000 mm. On figure 2.6, these mirrors are indicated by 'S'. The

![Figure 2.6. Schematic of the femtosecond laser system at the Rutherford Appleton Laboratory. The elements of the laser are labelled thus: Faraday Isolator (FI), concave mirror (CM), spherical mirror (M), Pockel's Cell (PC) and gratings (G1 - G4).](image-url)
preamplified pulse train is then removed from the amplifier and passed through a Pockel’s Cell (PC in figure 2.6). Pulses are selected from the 82 Mhz pulse train at a repetition rate of 10 Hz. The selected pulses are then re-injected into the amplifier for another five passes through the Ti:S crystal. The whole amplification process raises the pulse energy to 4 mJ in a pulse of 180 ps. The amplified stretched pulses then enter a compressor, consisting of a pair of 1500 lines/mm gratings in parallel arrangement (G3 and G4 in figure 2.6). This compresses the pulses back to $\tau = 50$ fs, with a pulse energy of 1 mJ. Optical losses are unavoidable in the compression process, mainly due to degradation of the reflectance of the gratings. The output pulse shape is monitored on a scanning autocorrelator, which receives the output of a 10% beam-splitter placed in the path of the oscillator pulse.

2.3.2 Beam transport and monitoring

Figure 2.7 is a schematic of the optics used to transport of the laser pulses to the spectrometer. The mirrors used throughout the present work are all gold-film on a glass substrate, which have the highest reflectivity for 790 nm laser light (~93%). To minimise optical losses, the number of mirrors is kept to a minimum.

Following compression, the laser pulses have linear polarization, with the electric field vector vertical, parallel to the axis of the TOFMS drift tube. However, the beam leaves the compressor 20 cm above the optical bench. A periscope is used to lower

-**Figure 2.7.** Top-down schematic of the beam transport optics. The elements present are: periscope (P), gold mirrors (M1 - M5), apertures (A), glass plate (GP), Integrating sphere (IS), photodiode (PD), half-wave plate ($\lambda/2$) and entrance window (W).
the beam as shown in figure 2.8. The arrangement of the mirrors in the periscope flip
the polarisation direction through 90°. This shall be referred to as ‘perpendicular’
polarization, as the electric field vector is perpendicular to the TOFMS axis.
A half-wave plate, mounted in a motorized rotation stage, controls the polarization
direction. This component is indicated by λ/2 in figure 2.7. A quarter-wave plate can
be inserted into the beam-path after the half-wave plate to produce circular
polarization.

Following optical losses from the mirrors and optical components, 900 μJ per pulse
is available at the entrance window. The laser pulses enter the vacuum system
through a fused-silica window (indicated by W on figure 2.1), which is mounted on
one of the 70 mm conflat ports on the vacuum chamber. The path of the laser pulses
is perpendicular to the axis of the TOFMS. On transmission though the entrance
window, we estimate a 10% temporal dispersion, hence the pulse length is around 55
fs in vacuum.

Pulse-to-pulse fluctuations in laser energy are monitored on a photodiode (PD). A
glass plate, indicated by GP in figure 2.7, is inserted into the beam path, which
transmits the majority (98%) of the pulse. The reflection generated by the glass plate
is then passed through an integrating sphere which insures that the photodiode
response is independent of polarisation direction. Typically, the laser pulse energy
fluctuates by of the order of 50%. The signal from the PD is used to produce a
trigger for the DSO, provided the PD signal is within ±10% of the user defined level
Typically, with the PD unsaturated and with a laser pulse energy of 900\(\mu\)J entering the TOFMS, the unsaturated PD signal had an amplitude of the order of 200 mV, with a full-width, half-maximum of 30 ns.

In a subsidiary experiment, the PD signal was measured with respect to the laser pulse energy (as measured with a calibrated pyrometer) directly in front of the TOFMS. It was found that the PD response was directly proportional to the laser pulse energy.

### 2.3.3 Beam focussing in vacuum

The laser pulses are focussed into the source region of the TOFMS, either by a parabolic mirror with a focal length of 2.2 cm, or by a spherical mirror with a focal length of 5 cm. The parabolic mirror is a glass substrate coated front and back with aluminum, mounted on a PTFE block, which is screwed directly to the bottom-plate of the TOFMS. The mirror is held onto the PTFE mount by way of two phosphor-bronze springs. Each of these springs is attached using two stainless steel M1.5 screws. A fine gold wire is attached to the back face of the mirror and to one of the phosphor-bronze springs, which is attached to earth to prevent electrostatic charging. Figure 2.9 is a schematic of the parabolic mirror and mount.

![Figure 2.9. Mount for the 1 cm diameter parabolic mirror.](image-url)
The spherical mirror is a glass substrate with an aluminum film deposited on a concave face. The mirror is mounted in a threaded stainless steel fitting, which is shown in figure 2.10. This mount is screwed directly into the cradle, and the position of the mirror adjusted until the focal spot is central to the axis of the spectrometer.

![Figure 2.10. Mount for the 2.54 cm diameter spherical mirror. S/S indicates stainless steel.](image)

Before time-of-flight data can be recorded, the optical axis of the spectrometer must be defined. This technique relies on the mechanical alignment of the mirror with the axis of the spectrometer (see figure 2.2). A low-power helium-neon (He-Ne) laser is expanded to a diameter of 1 cm using a telescope. This beam is directed into the vacuum system, and the reflected image of the mirror is observed. By moving the He-Ne beam so that the in-going path is central to the reflected image, the optical axis of the mirror is found. This position is checked using a 50% split of the He-Ne beam, reflected off the back face of the mirror. As shown in figures 2.9 and 2.10, the back face of both mirrors are planar, and are accessible from the exit window (see figure 2.1). With the optical axis of the apparatus established, two apertures are placed around the He-Ne beam. The positions of these apertures, A are shown in figure 2.7.
2.3.4 Calculation of focussed laser intensity

For the two different mirrors used in this work, calculations were made of the beam waist, \( \omega_0 \) (m) using the laser wavelength, \( \lambda \) (m) and beam diameter, \( D \) (m) along with the focal length of the mirror in question, \( f \) (m), as shown in equation 2.1.

\[
\omega_0 = \frac{2f\lambda}{\pi D}
\]

Equation 2.1

Similarly, calculations were made of the confocal lengths, \( z_0 \) (m) of the two different foci, according to equation 2.2.

\[
z_0 = \frac{2\pi \omega_0^2}{\lambda}
\]

Equation 2.2

An estimate was then made of the two different intensities, \( I \) within an Airy disk containing 86% of the pulse using equation 2.3. Here \( E \) is the pulse energy (900 \( \mu \)J), \( T \) is the transmission coefficient of the pulse through the optics in the system (0.9), \( L \) is the diffraction limit (1.5) and \( \tau \) is the pulse length (5.5 \( \times \) 10\(^{-15} \) s).

\[
I = 0.86 \times \frac{ET}{\pi \tau (L\omega_0)^2}
\]

Equation 2.3

For the 2.5 cm focal length parabolic mirror, \( \omega_0 = 1.3 \) \( \mu \)m, \( z_0 = 13 \) \( \mu \)m and \( I = 1.1 \) Wcm\(^{-2} \). For the 5 cm focal length circular mirror, \( \omega_0 = 2.5 \) \( \mu \)m, \( z_0 = 50 \) \( \mu \)m and \( I = 3 \times 10^{16} \) Wcm\(^{-2} \). Clearly, the shorter focal length parabolic mirror has a much sharper focus, generating far higher intensities.

2.3.5 Calibration of focussed laser intensity

It is necessary to test the accuracy of the calculations in section 2.3.2, so as to confirm the conditions in the focal volume. As discussed in chapter 1, Augst et al (1989) employed a time-of-flight technique similar to that employed in the present work to measure the number of stages of ionisation of the five noble gases (He, Ne, Ar, Kr and Xe). As in equation 2.3, focussed laser intensity is dependent on the pulse energy, temporal width and the focal spot size. To calibrate the absolute laser intensity in the present work, argon and xenon were introduced independently into the TOFMS as described in section 2.2.3 to a background pressure of 1 \( \times \) 10\(^{-7} \) mbar. The laser pulse energy was measured immediately before entering the TOFMS, and was found to be 900 \( \mu \)J. Time-of-flight spectra were recorded for argon and
Figure 2.11. Time-of-flight spectrum of argon, recorded with the spherical mirror, indicating ionization up to $\text{Ar}^{7+}$, corresponding to an intensity $> 3 \times 10^{16}$ Wcm$^{-2}$.

Figure 2.12. Time-of-flight spectrum of xenon, recorded with the spherical mirror, indicating ionization up to $\text{Xe}^{8+}$, corresponding to an intensity $> 8 \times 10^{15}$ Wcm$^{-2}$.

xenon using this technique. These spectra are shown in figures 2.11 and 2.12 respectively. There is a good agreement between the calculated and experimental
intensities.

2.4 Data collection techniques

Three related techniques have been employed in the present work, all based on the TOFMS system. Firstly, straightforward time-of-flight mass spectroscopy has been used, where the DSO averages the ion signal over a large number of laser shots. Secondly, covariance mapping is used to identify the Coulomb explosion channels. Finally, Ion-Momentum Imaging has been used to investigate the geometry of the exploding molecule.

2.4.1 Behaviour of ions in the spectrometer

The behaviour of an ion following production depends both on the magnitude of the momentum (or kinetic energy) of the ion and the direction in which it is initially travelling. If an ion is generated with zero momentum (hence zero kinetic energy), the total flight time of that ion will depend purely on the charge-to-mass ratio and the extraction field used. The equations of motion of ions with mass \( m \) (amu) and charge \( q \) (au), with momentum \( p \) (amu ms\(^{-1}\)), initially travelling at an angle \( \theta \) (degrees) to the axis of the spectrometer have been calculated from Newtonian mechanics. These equations are shown in appendix 2. These equations allow the total flight time of an ion to be calculated.

![Time-of-flight spectrum of carbon dioxide recorded at an intensity of 3 \times 10^{16} \text{Wcm}^{-2}, with an extraction field of 300 V.](image-url)
Ion identification is possible as the total flight time is inversely proportional to the square root of the charge-to-mass ratio of the ion in question. Figure 2.13 is a typical time-of-flight spectrum of carbon dioxide. To illustrate the ion-identification process, the time-of-flight of the various ion-signal peaks is plotted against the square root of the charge-to-mass ratio as illustrated in figure 2.14. The points generated by this process are fitted with a $y=ax+b$ linear fit, where $y$ is $\sqrt{(m/q)}$ and $x$ is the time-of-flight in seconds. Constants $a$ and $b$ are the gradient and intercept of the linear fit. In the case of figure 2.15, $a=2.705\times10^6$ and $b=0.369$. As can be seen, the quality of the fit of the experimental data to the linear relationship shows that the operation of the spectrometer can be accurately quantified.

The behaviour of energetic ions is more complex, as the orientation of the initial momentum vector with respect to the spectrometer axis modifies the arrival time of the ion. If an ion is generated with non-zero momentum parallel to the spectrometer axis, ‘forwards-backwards’ peaks are generated. Figure 2.15 indicates how these peaks are produced. Ions with a momentum component in the direction of the detector arrive earlier than ions with zero momentum. In figure 2.15, this process is indicated by the ion with initial momentum $p_1$. Similarly, ions with a momentum component in the opposite direction to the detector are detected later than ions with
zero momentum: see ion with initial momentum $p_2$ on figure 2.15. The momentum resolved by the spectrometer is proportional to the time difference between the zero momentum point and the peak in the ion signal, as shown in equation A2.8. Similarly, the kinetic energy of the ion is related to this time difference by equation A2.9.

Ions generated with zero momentum parallel to the spectrometer axis but with a significant component perpendicular to this axis are detected as ions with zero momentum. This is because the present detector can only measure the component of the momentum in the direction of the detector. However, the ion will not be detected if the momentum perpendicular to spectrometer axis is sufficient to carry it either to the wall of the drift tube or outside the diameter of the aperture (if present).

![Illustration of the behaviour of energetic ions within the spectrometer.](image)

**Figure 2.15.** Illustration of the behaviour of energetic ions within the spectrometer.

### 2.4.2 One-dimensional time-of-flight mass spectroscopy

The simplest method used to investigate the Coulomb explosion process is one-dimensional time-of-flight mass spectroscopy. The spectrometer is filled with the target gas to around $1 \times 10^{-7}$ mbar (as measured with the ionisation gauge). The
detector signal is then averaged over a large number of laser shots on the DSO using the 'average' acquisition mode (see appendix A3.1 for details). The time-of-flight spectra shown in figures 2.11 to 2.13 were collected in this manner.

2.4.3 Covariance mapping

In the laser-molecule interactions studied in the present work, the laser intensity is sufficient to multiply ionise the molecule within the rising edge of the pulse. This ionisation is spread across the molecule, hence a triatomic molecule ABC ionised six times within the laser pulse will Coulomb explode into A^{2+} + B^{2+} + C^{2+}. This type of process is usually described in the following manner: ABC → ABC^{L+} → A^{M+} + B^{N+} + C^{P+}, where L = M + N + P. Consequently, this channel is the (M, N, P) channel. The one-dimensional time-of-flight technique is sufficient to identify the species of ion produced in the interaction of the laser pulse with the target gas. In the case of diatomic molecules (see for example figure 1.33 as published in Ellert et al. 1998) the Coulomb explosion channels can be identified directly from the one-dimensional TOF spectrum. This is because there is little overlap in momentum for the different explosion channels, and conservation-of-momentum can be applied directly. However, in the case of molecules with three or more atomic constituents, the different channels produce ions of a larger range of momenta. Hence, the one-dimensional TOF technique cannot be used to unambiguously identify the Coulomb explosion channels present. In the Coulomb explosion of carbon dioxide, doubly-charged oxygen ions may be produced by a number of different explosion channels. The average momentum of the O^{2+} ions from these different processes is different; however, the distribution of momenta produced causes a large overlap within the O^{2+} ion peak. These sort of processes can be resolved by coincidence techniques. However, this technique requires a count rate of one or less Coulomb explosion per laser shot, hence is an ineffective use of laser time. Furthermore, extensive post-processing of the data is required. These problems can be overcome using the covariance mapping technique (Frasinski et al. 1989, 1994). By collecting time-of-flight spectra individually (rather than averaging over a large number of laser shots), the dynamics of the Coulomb explosion process can be recreated. If the count rate is low (3-4 explosions per laser shot), calculating the covariance coefficient over a large number of shots reveals the Coulomb explosion
processes taking place in the explosion.

The covariance coefficient, $C$, is defined as shown in equation 2.4. Variables $x(t_1)$ and $y(t_2)$ are the signal strength at times $t_1$ and $t_2$ in the time-of-flight spectra.

$$C(t_1, t_2) = \langle x(t_1)y(t_2) \rangle - \langle x(t_1) \rangle \langle y(t_2) \rangle$$

Equation 2.4

This equation can be rewritten as shown in equation 2.5.

$$C(t_1, t_2) = \frac{1}{N} \sum_{i=1}^{N} (x_i(t_1)y_j(t_2)) - \frac{1}{N^2} \sum_{i=1}^{N} x_i(t_1) \sum_{j=1}^{N} y_j(t_2)$$

Equation 2.5

The first sum on the right-hand side of equation 2.5 is the average of the vector multiplication of the two one-dimensional TOF spectra, and the second sum is the vector product of the averages of the two one-dimensional spectra.

The ion signal can be the same TOF spectrum, as in the present work, hence $x = y$ in equations 2.4 and 2.5, or can be the output of a second detector. For example, Prasinski et al (1992) used two coaxial detectors: one was a ion TOF detector similar to that used in the present work, and the other was an electron TOF detector. It is necessary to calculate the covariance coefficient for each pair of TOF points, as the correlation between events is not known before the experiment is performed.

Figures 2.16 and 2.17 illustrate the calculation of the two elements of the covariance coefficient ($\langle xy \rangle$ in figure 2.16 and $\langle x \rangle \langle y \rangle$ in figure 2.17).

Figure 2.16. Illustration of the calculation of $\langle xy \rangle$ for $N$ spectra. For each individual pair of spectra, the cross product is formed. This is then averaged over all $N$ spectra.
Figure 2.17. Illustration of the calculation of $<x><y>$ for N spectra. First, the average spectra are calculated by averaging the signal at each time $x(t)$ and $y(t)$, then the cross product of these average spectra is formed.

Figure 2.18 is a covariance map of carbonyl sulphide (OCS) recorded at an intensity of $3 \times 10^{16}$ Wcm$^{-2}$ with 55 fs laser pulses at $\lambda = 790$ nm. The x- and y-axes are ion time-of-flight in seconds, and the z-axis is the covariance coefficient in arbitrary units on a colour scale. The pairs of correlated events are the islands of positive covariance coefficient. An average TOF spectrum is shown along the x- and y-axes. The ions are identified using the method described in section 2.4.1, i.e. the zero-momentum point is identified, and ion time-of-flight is converted into momentum using the equations of motion of ions in the spectrometer – see appendix 2. Clearly,
for each point on the covariance map, there are two corresponding ion momenta for the x- and y-axes. Therefore, each correlation on the map identifies a pair of ions. As triatomic molecules are being examined in the present work, it is necessary to use conservation-of-momentum to correlate pairs of covariance 'islands'. The correlations appear as pairs of islands, as for a particular process, there is a forward-backward correlation and a backward-forward correlation. Comparing the momenta of all of the pairs of correlation islands then identifies the Coulomb explosion channels.

As a low count rate is required for the covariance technique to function correctly, a low target gas pressure is required. Typically, a gas pressure of $3 \times 10^{-9}$ mbar is used. Furthermore, when collecting covariance data, a range of extraction fields is used to examine areas of the mass spectrum in detail.

The LabVIEW software used to process the TOF data and generate the covariance maps will be discussed in chapter 3.
2.4.4 Ion-Momentum Imaging

The geometry of the exploding molecule may be quantified using the covariance mapping technique (see for example Comaggia 1996 and section 1.6.1). However, without the use of a position- and time-sensitive detector, a large amount of information about the angular dependence of the explosion process is lost. By combining the speed and efficiency of the averaging TOF technique with the explosion channel information gained from the covariance technique, the Ion-Momentum Imaging (IMI) technique allows the geometry of the exploding molecule to be inferred.

The data collection methods employed as the first stage of the IMI technique is similar to the MRMI technique of Hishikawa and co-workers (see section 1.6.2). However, the data correction and simulation methods are different, hence the distinction will be made between the present work and that of Hishikawa by using the two abbreviations. The two main steps of the IMI technique are data collection and data correction, as discussed below. Unlike covariance mapping, the data collection method for IMI uses high target gas pressure in the interaction region of the spectrometer, which insures a high count-rate. It is therefore not necessary to use as large a number of laser shots as compared to the covariance technique. Typically, a target gas pressure of $10^7$ mbar is used.

2.4.4.1 IMI data collection

To quantify the behaviour of a molecule in the laser field, the ion signal is measured as a function of polarization direction by rotating the half-wave plate before the entrance window into the vacuum system ($\lambda/2$ in figure 2.7). Two types of rotation stages were used in the present work. The first experiments of this type were performed with a rotation stage that rotates at a constant rate of 0.1 degrees per second (on loan from the University of Reading). As the polarisation direction rotates at twice the rate of the half-wave plate, the electric field direction rotates at 0.2 degrees per second. Time-of-flight spectra are recorded for 100 laser shots. Since the laser operates at 10 Hz, the laser polarisation direction rotates by 2 degrees in this time. The time taken for the half-wave plate to rotate through 360° ten times was measured, giving the rotation frequency. To synchronise the data collection with the
half-wave plate, the absolute time is recorded at the start of each experimental run, and after each average spectrum is complete, the time is recorded again, then the total amount of rotation calculated.

This system has one drawback. If the average laser pulse energy changes during an experimental run, the DSO run t trigger will not be at 10Hz; hence, the half-wave plate will rotate through more than 2 degrees. This will produce data in unequal angular steps. To combat this problem, a computer controlled rotation stage was used.

The half wave plate was mounted in a Newport URM-100CCHL rotation stage. The motion of this device is governed by a Newport MM-4005 control unit, containing a Newport OPT7G interface card. An RS-232 link was used to interface the control unit to the PC interfaced with the DSO. This means that one computer can synchronise the data collection and the position of the half-wave plate. In other words, the PC starts data collection on the DSO, waits for collection to finish, then moves the half-wave plate by some pre-set interval, then restarts data collection. Following a 360-degree rotation of the polarisation, all recorded spectra are sequentially recalled to form a time-of-flight matrix.

![Figure 2.19. TOF matrix of nitrous oxide recorded with 790 nm 55 fs laser pulses focused to generate an intensity of $3 \times 10^{16}$ Wcm$^{-2}$. The position of the N$_3^+$ ion is indicated for later discussion.](image)
An example of a TOF matrix is shown in figure 2.19. Information about the geometry of the exploding molecule can be inferred from the TOF matrix, but the results are more meaningful when presented as an ion-momentum image. Displaying a sub-matrix of the signal from a particular ion over all angles as a three-dimensional polar plot creates an ion-momentum image (IMI). The start (or zero) point of the matrix is the zero momentum point for the ion in question (see section 2.4.1 for discussion of the zero-momentum point) to some pre-determined maximum momentum. This maximum, referred to as $P_{\text{max}}$, is chosen such that all atomic ions can be displayed over the same momentum range. Figure 2.20 illustrates this process.

Figure 2.21 is an IMI plot generated from the TOF matrix in figure 2.19: this is the N$^{3+}$ ion, and is the green signal on the left-hand side of the matrix.

2.4.4.2 IMI data correction procedure

Following the collection of the "raw" IMI data, the instrumental effect is removed from experimental data. The true dependence of the ion signal on momentum and polarisation direction is only evident after this correction.
To generate TOF matrices and IMI plots, it is vital that the detector has good angular resolution. Hence, when recording TOF matrices, the aperture is used. This reduces the angular acceptance, $\varphi_{\text{ACC}}$ of the spectrometer, hence improves the angular resolution. However, by reducing the angular acceptance of the detector, there is considerable variation of collection efficiency with ion momentum and species.

Figure 2.21. Uncorrected IMI plot for the $N^{3+}$ ion from the Coulomb explosion of $N_2O$, generated from the TOF matrix presented in figure 2.19.

Figure 2.22. The trajectories for two ions making the same initial angle to the detector axis, but with different momentum magnitudes. The ion following trajectory $T_1$ passes through the aperture hence is detected, whereas the ion following trajectory $T_2$ is not.
There is an enhancement of the ion signal for low momentum ions with respect to high momentum ions, as the low momenta ions are preferentially detected. This process is illustrated in figure 2.22. Two ions (A$^+$ and B$^+$) are produced with initial momenta $p_1$ and $p_2$ respectively. The angle between each of the momentum vectors and the axis of the spectrometer are the same. In this case, $p_1 < p_2$, which results in ion A$^+$ being detected, as it passes through the aperture after following trajectory $T_1$. However, ion B$^+$ follows trajectory $T_2$, and is undetected.

The correction geometry to be considered is presented in figure 2.23. This correction method accounts for the range of momenta that may contribute to the signal, I, of an ion with momentum $p$. By reducing the geometry of the TOFMS to its simplest equivalent form, an ion with momentum $p'$ and initial angle $\gamma$ with respect to the axis of the TOFMS (where $p' > p$ and $\gamma > 0^\circ$) can contribute to the signal of the ion with momentum $p$, thus $p' \cos \gamma = p$. This is because the detector only resolves the component of $p$ parallel to the axis (as discussed in section 2.4.1). By calculating the maximum angle $\alpha$ at which any ion will pass through the aperture with momentum $p/\cos \alpha$, and scale $I$ at $p$ by the ratio $C$ of the area $S$ to the area of the hemisphere of radius $p/\cos \alpha$. The area $S$ is defined by the rotation of $p \tan \alpha$ over all azimuthal angles. This correction factor is referred to as the ‘finite angle’ correction, as there is a finite angle that the initial momentum of an ion may make to the TOFMS axis and contribute to the TOF spectrum. The correction factor reduces to $C = q \sin^2 \alpha$, where $q$ is a constant of proportionality. This process is summarised in equation 2.6

$$C = \frac{S}{2\pi r^2} = \frac{\pi (p \tan \alpha)^2}{2\pi (p/\cos \alpha)^2} = q \sin^2 \alpha$$

Equation 2.6
Figure 2.24. Dependence of the finite angle correction with ion momentum for the O$^{2+}$ ion. Also presented is the variation of a simple correction derived by considering only the maximum acceptance angle.

The functional form of the finite angle correction is shown in figure 2.24 for the O$^{2+}$ ion. Also shown in figure 2.24 is the variation of a correction derived simply by considering the solid angle of the maximum acceptance angle for an ion with momentum $p$. The intuitive solid angle correction is unphysical, as for low

![Graph showing the dependence of the finite angle correction on ion momentum for O$^{2+}$ ion.]

Figure 2.25. Corrected IMI plot for the N$^+$ ion generated by the Coulomb explosion of N$_2$O. By comparing this figure and the IMI plot in figure 2.20, the effect of the finite angle correction is seen.
momentum (for O\textsuperscript{2+}, low momentum is $p < 3 \times 10^4$ amu ms\textsuperscript{-1}), the correction is independent of momentum.

The effect of applying the finite angle correction to the raw IMI data in figure 2.21 is shown in figure 2.25. The relative strengths of the low and high momentum features are altered.
Chapter 3. Data acquisition and analysis

3.1 Introduction

This chapter will discuss the techniques used to collect, process and store time-of-flight data. Firstly, a brief summary of the LabVIEW programming environment is given followed by a description of the digital storage oscilloscope (DSO) used to measure the ion signal from the detector. The interface between the DSO and a laboratory PC is described followed by a description of the interface between the PC and the optic control device. To allow an understanding of the software behind the present work, a description is then given of the LabVIEW software used to process and analyse the different data types collected in the present work. Finally, the mechanics of the Monte Carlo method are described.

3.2 LabVIEW summary

LabVIEW is a software development environment, using a graphical programming language, G to create programs in a block diagram form. LabVIEW programs are referred to as ‘virtual instruments’ (VI’s) because their appearance and operation imitate actual instruments. Central to the creation and operation of VI’s is understanding the way in which the user constructs and interacts with the VI. Each VI has an interactive user interface, called the ‘front panel’, which is displayed in one window. Input is through ‘controls’ (switches, numerical displays and menus) and output is through ‘indicators’ (indicator lights, numerical displays and graphs). Information is passed from the front panel to the ‘block diagram’, which is constructed in G. The block diagram resembles a circuit diagram, and is equivalent to the source code of a conventional program. ‘SubVI’s’ are created by placing one VI onto the block diagram of another VI, hence creating a subroutine.

Writing VI’s in LabVIEW revolves around the two ‘palettes’ used to select elements to be placed on the front panel or the block diagram. The ‘controls’ palette contains all the elements that can be placed onto the front panel, from switches to graphical displays. The ‘functions’ palette contains all the ‘nodes’ that can be placed on the block diagram. Most of these nodes consist of pre-written functions, such as the ‘numerical’ sub-palette, containing, for example, mathematical operators and trigonometrical functions.

The construction of a VI involves placing controls on the front panel. Nodes relating
to these inputs then appear on the block diagram. Data appearing in the front panel controls is then available on the block diagram. This data is then processed on the block diagram, and the output passed to indicators on the front panel.

An example LabVIEW VI is shown in figure 3.1, which is used to generate a standard Gaussian function. The front panel is show in figure 3.1(a), with the controls for the VI down the left hand side. The start ($x_{\text{min}}$) and stop ($x_{\text{max}}$) of the waveform can be controlled, as can the resolution ($n_{\text{pts}}$) and the mean $\mu$, and standard deviation $\sigma$. The block diagram is presented in figure 3.1(b), showing the calculations performed using the inputs from the front panel. The resulting waveform is displayed in the right hand side of figure 3.1(a).

![Figure 3.1](image.png)

**Figure 3.1.** Illustration of a LabVIEW VI, used to generate a Gaussian function of arbitrary resolution. (a) The front panel and (b) the block diagram.
The way in which nodes on the block diagram are connected dictates data flow. Unlike ‘top-down’ languages such as Fortran and C++, LabVIEW VIs execute in the order in which data becomes available. In other words, once all of the inputs into a node or subVI are satisfied, the node will execute. In general, this capability makes LabVIEW very efficient. However, at times it is necessary to constrict the order of execution of a VI. For example, when communicating with the DSO, it is necessary to ensure that the waveform acquisition commands are sent in the right order.

The LabVIEW environment was chosen for three main reasons. Firstly, it is designed specifically for data collection and processing, and as such, removes memory management concerns. Secondly, unlike more traditional languages (C, Fortran), LabVIEW VIs are both straightforward to construct and understand. Finally, the environment is equipped with an extensive mathematical suite, reducing coding time for analysis routines.

3.3 Data acquisition

The elements of the data acquisition system are described in the following sections. This discussion focuses on the DSO functions utilised in the present work, and briefly describes the elements of the DSO-to-PC interface.

3.3.1 Tektronix TDS 744A digital storage oscilloscope

The ion signal is recorded on a Tektronix TDS 744A, which is a four-channel digital storage oscilloscope (DSO), with a maximum temporal resolution of 500 ps. The ion signal is digitised in discrete intervals. The sampling interval is of the order of 20-times smaller than a standard channel plate pulse, hence the TOF signal is effectively continuous.

The oscilloscope is menu-driven, to allow quick access to the numerous features, and can be fully-computer controlled. The full specifications of the TDS 744A are given in appendix 3. For simplicity, from this point on, the TDS 744A will be referred to as the DSO.

Figure 3.2 is a schematic of the left-hand side of the front panel of the DSO, and the right-hand side is shown in figure 3.3. The DSO is operated using the ‘menu selection controls’, shown on figure 3.3. Each of these controls brings up a menu on the DSO display, which is in the centre of figure 3.2. The exception is the ‘run/stop’ button, which is used to start data collection. The ‘main menu buttons’, shown on
figure 3.2, are then used to bring up a number of side menus, controlled by the ‘side menu buttons’. The way in which the waveform is displayed is governed with the ‘vertical’ and ‘horizontal’ controls. These controls are labelled on figure 3.3. Each channel is activated using the ‘channel selection controls’.

Data signals are connected to the DSO through the four BNC inputs on the front panel, shown in figure 3.3. The impedance (50Ω or 1MΩ) and coupling (AC, DC or GND) for each of these channels is controlled using the ‘vertical’ menu. The channel recording the ion signal is set to 50Ω impedance, and the photodiode channel set to 1MΩ.
An example of the DSO display is shown in figure 3.4. The main and side menus are visible along the bottom and to the right of the display.

Along the top edge of the waveform display are the ‘acquisition indicators’. The ‘run/stop’ indicator shows the state of the DSO. Once data collection is started, the DSO can either run until the ‘run/stop’ button is pressed again (‘stop after run/stop button’ mode), or until a user-defined number of acquisitions have been collected (‘stop after single sequence’ mode). The operation mode of the DSO is shown in the ‘stop after’ indicator. Also included in the ‘acquisition indicators’ is the horizontal sampling rate in samples per second (S/s). The other indicators shown in figure 3.4 show the horizontal and vertical scaling parameters, along with the trigger parameters.

Figure 3.4. Annotated display from the DSO.

Figure 3.5. Schematic of the back panel of the DSO.
The back panel of the DSO is shown in figure 3.5. There are two bus connectors, namely the RS-232 and the GPIB (General Purpose Interface Bus). Data transfer between the DSO and a PC is possible over either of these ports, however the transfer rate over the GPIB is considerably higher than the RS-232 (1.4 Mbytes/s for the GPIB, 19,200 bits/s for the RS-232).

3.3.2 DSO to PC interface via GPIB
The DSO can store waveforms on a 3½ floppy disk, as shown in figure 3.2. However, manually recording a large number of waveforms is an inefficient use of laser time. By interfacing the DSO with a laboratory PC, waveform collection and storage can be performed automatically. This communication is performed over the GPIB because of the considerably higher data transfer rate as compared to the RS-232.

The elements of the DSO – PC link are an AT-GPIB/TNT card for Plug and Play ISA (National Instruments p/n 776943-01) and a Type X2 double-shielded 2-metre GPIB cable (National Instruments p/n 763061-02). This card and cable operate using the ANSI (American National Standards Institute) IEEE Std 488.2 GPIB protocol. The GPIB card is fitted into the ISA port of a Dell Optiplex 560/L desktop PC with a 60 MHz Intel Pentium processor. The physical memory of this PC has been upgraded to 40 Mbytes to allow it to operate using Microsoft Windows 95. The DSO and the PC are then connected using the cable. Both the PC and DSO must be switched off when this is done. If this connection is made whilst either the PC or DSO are turned on, the communications will not function.

3.3.3 Setting DSO GPIB parameters
Before communication between the DSO and PC can be established, both the DSO and the PC must be configured to ‘talk’ and ‘listen’ through the same bus. This is done through the ‘Utility’ menu (see figure 3.3). The instrument should then be given a unique address. In the present work, the DSO is set as address 1. This must agree with the settings in any LabVIEW communication VI.

3.3.4 Basic DSO – PC interface protocol
The DSO can respond to two different types of ASCII input, namely ‘commands’ and ‘queries’. A command is used to instruct the DSO to perform an operation, for
example to record a waveform or activate a particular channel. A query is used to request information from the DSO, for example to ask the sampling frequency of a particular channel. Generally, a query ends in a ‘?’ character.

An example of a command is the ‘ACQuire:STATE RUN’, which is equivalent to pressing the ‘Run/Stop’ button (see figure 3.2) which starts data collection. Similarly, the query ‘ACQuire:STATE?’ asks the DSO whether it is collecting data or not. If the DSO is collecting, the ASCII string ‘ACQuire:STATE 1’ is sent across the GPIB.

The ASCII strings sent to the DSO can be in either of the following formats. The full command can be sent - from the first example above, this would be ‘acquire:state run’. Alternatively, the mnemonic form can be used, which makes the commands more concise. From above, this reduces to ‘acq:state run’. The mnemonic part of the command or query is indicated in capital letters. A complete list of the ASCII commands and queries used in the present work are given in appendix 5.

The DSO-PC communication is summarised as follows. Before a waveform can be transferred, the ‘DATa:SOURce’ command is used to instruct the DSO which waveform is required. The ‘WFMPRe?’ query is then used to request the waveform formatting data, such as the horizontal sampling frequency and number of points in the waveform. The ‘CURVe?’ query is then sent to the DSO, which then sends the waveform across the GPIB. The waveform can be sent either in binary or ASCII format. In the present work, RP binary encoding is used, where the data is represented as a positive integer, where the MSB (Most Significant Bit) is transferred first. The encoding method does not change the resolution of the waveform when it has been decoded on the PC. Clearly, the encoding and decoding method used must agree between the DSO and PC.

3.3.5 Data storage

With the ASCII data transferred, the spectrum is stored on the hard disk of the PC. The data could be stored as transferred, which is space-efficient. However, this format is incompatible with other Windows utilities that might be used to present or analyse the data. Therefore the data is saved as a two-column text file, where column 1 is the time in seconds, and column 2 is the potential in volts. To convert the ASCII data into a useable format, the horizontal and vertical scaling parameters transferred in response to the ‘WFMP?’ query are used to format the raw data.
The LabVIEW environment is fully integrated with the Windows operating system, hence spectra can be stored in a shared folder on a remote computer, either through the Network Neighbourhood in Windows, or through a FTP client. This facility has proved useful while collecting data at the Rutherford Laboratory, as it has allowed data analysis to be performed at University College shortly after it is recorded at RAL.

When performing ion-momentum imaging or covariance mapping, it is necessary to store spectra repeatedly. To accelerate the storage process, spectra can be automatically placed into a folder, named with the experimental parameters described above. Each individual spectrum is then named according to the laser polarisation direction (in the case of ion-momentum imaging) or the spectrum number (in the case of covariance mapping). This method shall be referred to as 'sequential storage'.

This process is reversed when creating ion-momentum images. In sequential or bulk recall, the user selects a directory, then the software reads the filenames of the spectra within the directory, then recalls them in the correct numerical order.

3.4  **Newport MM-4005 Motion Controller**

As described in section 2.4.4.1, ion-momentum imaging is performed using a Newport URM-100CCHL rotation stage driven by a Newport MM-4005. The Newport MM-4005 is also connected to a MFN-25CC translation stage, used to control one arm of an interferometer (see appendix A7.5), or to change the lens position in order to perform z-scan measurements (see appendix A7.9). The rotation stage can also be used as a pulse energy selector, by placing the rotation stage containing the half-wave plate before the compressor. The compressor is polarisation dependent, hence by rotating the polarisation direction the transmitted energy varies.

Communication between the Newport controller and the PC is by ASCII commands. However, unlike the DSO, the Newport is controlled over the RS-232 bus, to avoid communication conflicts. With the Newport controller, only commands are sent to move a specific stage to a specific position. The ASCII commands used with the Newport are shown in appendix 5.2.

3.5  **Laser pulse energy gating procedure.**

The DSO may be triggered by any of the four channels on the front panel, or by the
auxiliary trigger input on the back panel. Before collecting TOF data, the triggering of the DSO must be established. In the present work, the trigger signal was connected to channel 1, carrying a start pulse generated by the laser. The start pulse was generated by a small percentage (~2%) of the pulse energy being split from the main beam (see figure 2.7). However, given the 50% fluctuation in the laser pulse energy, it was necessary to 'gate' the ion signal with the photodiode output.

The gating was set up using the following procedure.

1. Place calibrated pyrometer in the laser path, and measure the laser pulse energy on the DSO. The pulse amplitude may be measured using the cursors or the measure facility. The DSO can be triggered either from the pyrometer signal or from the Pockel's Cell signal, and should be 'edge' triggered.

2. Remove the pyrometer from the optical path, and measure PD signal on DSO, triggering from Pockel's cell signal. Ensure PD signal is not saturated, indicated by a broad (>50 ns) tail, and that the correct impedance is used (1 MΩ).

3. Average the PD signal over 100 laser shots and measure pulse amplitude using the cursors. If the amplified PD signal strength is low (<50 mV), amplification may be necessary. Calculate the maximum and minimum limits for the laser pulse energy. Typically, a ±10% window is used.

4. The DSO is now switched to 'runt' triggering, and the upper and lower levels are set to the limits calculated above. The channel displaying the PD signal may now be switched off.

3.6 Data collection and processing: covariance mapping

The use of covariance mapping has been introduced in chapter 2. In this chapter, the data collection considerations of this technique shall be discussed. The covariance technique can be segmented into five processes, described in the following sections.

3.6.1 Data collection

As it is necessary to retain the shot-to-shot variation of the ion signal, the DSO is operated in 'hi-res' mode, which improves the sampling resolution of a single shot TOF spectrum. Furthermore, to minimise the communication time between the DSO and the PC, the 'FastFrame' feature was used, which groups successive spectra into one continuous single spectrum. The number of points per spectrum is set to 50,000,
3.6.2 Data processing

There was an instrumental 'ringing' on the channel plate output. The main pulse was followed by a series of high frequency oscillations that decay over around 100 ns. An example of a channel plate pulse is shown in figure 3.6. The oscillations had a constant period of between 11 and 12 nanoseconds, which is equivalent to a frequency of approximately 80Mhz. The detector circuit was rebuilt to try to eliminate this unwanted signal, but to no avail. However, a method to remove this effect from the data was developed, following the transfer of the data to the PC. Firstly, a peak detection routine was used to find the main signal peaks throughout the channel plate signal by setting a threshold voltage. The desired part of the signal is then removed from the ringing signal by examining each peak found by the peak detection routine. Each data point which has a y-value greater than zero is placed into an empty array of the same length as the original array. This process is illustrated in figure 3.6. After the application of the ringing filter, the channel plate signal consists of single peaks. All other values are set to zero.

![Figure 3.6. Illustration of the peak detection process.](image)

3.6.3 Calculation and display of the covariance coefficient

Each FastFrame spectrum is broken into 20 single shot spectra. The covariance coefficient (see section 2.4.3) is then calculated for each spectrum, generating a two-dimensional array 250 x 250 points. The average of all of these 20 arrays is then
calculated. One covariance map is generated for each FastFrame. The covariance map from the current map is weighted according to the total number of spectra recorded. This weighted map is then added to all of the previous maps. The covariance map is then displayed in three-dimensions as an intensity plot, where the covariance coefficient is represented by a colour scale. An example of such a display has been presented in figure 2.18.

3.6.4 Storage
When a sufficient number of laser shots has been recorded (typically 10,000), the data collection process is stopped, and the covariance map is stored as a two-dimensional comma delimited array. The averaged time-of-flight spectrum is also stored with the map, as two extra columns, added to the array. Covariance maps may be stored using the network storage methods described in section 3.3.5.

3.7 Data collection and processing: ion momentum imaging
The mechanics of the ion momentum imaging technique have been described in chapter 2. This section will deal with the data processing concerns of this technique. The generation of a momentum map from the TOF matrix is described, with particular reference to the conversion between Cartesian and polar co-ordinates. The application of the finite angle correction is then discussed.

3.7.1 Data collection
The DSO was operated in average mode, with the number of averages set to 100, and the number of points per spectrum set to 5000. Once the DSO had completed an average of the TOF signal, the data was transferred to the PC, then the half-wave plate in the rotation stage is rotated by one degree. Spectra are stored using the sequential storage method, where the filenames assigned to the spectra are the half-wave plate angle with respect to the starting position.

3.7.2 Generating a time-of-flight matrix.
Once the half-wave plate has been rotated through 180° in 1° steps (hence rotating the polarisation direction through 360° in 2° steps), the 180 averaged TOF spectra are recalled in bulk. The ion signal (column 2) from each of the spectra is read, and
placed into a 180 × 5000 point array. This is the TOF matrix, a Cartesian display of
the ion signal for all time and angle as shown in figure 2.19. Each position within
this matrix therefore corresponds to a unique time-of-flight in seconds and angle
between the polarization direction and the detector axis in degrees.

3.7.3 Conversion from TOF matrix to Ion-Momentum Image
As discussed in chapter 2, the TOF signal as a function of laser polarization direction
can give useful insights into the behaviour of the exploding molecule when displayed
as a TOF matrix. However, the data is more easily understood when presented as a
three-dimensional polar plot, which in the present context is referred to as an ion-
momentum image.

The transformation necessary to convert from the TOF matrix to the IMI map is
shown in figure 3.7: it is a basic Cartesian-polar transformation. However, LabVIEW
can only display data as a Cartesian intensity array, hence it was necessary to write
the software to perform this transformation from scratch.

The first step in the IMI-generation routine is to define an empty array into which the
raw TOF data is to be placed. The size, hence resolution of the empty IMI array is
defined by \( x_{\text{dim}} \) and \( y_{\text{dim}} \), as illustrated in figure 3.8. For the purposes of the following
discussion, \( x_{\text{dim}} \) and \( y_{\text{dim}} \) can be different values, however, the horizontal (x) and
vertical (y) resolutions are generally the same. Two important points within the
empty IMI array are the origin (0 in figure 3.8), and the centre of the array (shown
by the thick black lines).

The next step is to select the subset of the TOF matrix to be converted to an IMI plot.
This is done using the ‘start’ and ‘stop’ cursors on the front panel of the ‘normalization
and polar plotting.vi’ as shown in appendix 4. These cursors define the times
corresponding to \( p_0 \) and \( p_{\text{max}} \) as shown in figure 2.20. The time to momentum

![Figure 3.7. Illustration of transformation from TOF matrix to IMI plot.](image)
conversion is through equation 3.1.

\[ p(\Delta t) = k q e \Delta t \]  

Equation 3.1

Next, using the range of momenta \( p_o \) to \( p_{\text{max}} \), each point on the empty IMI plot (figure 3.8) corresponds to an angle \( B(i,j) \) and momentum \( p(i,j) \) defined by:

\[ B(i, j) = \tan^{-1}\left( \frac{j - y_{\text{dim}}}{i - x_{\text{dim}}} \right) \]  

Equation 3.2

\[ p(i, j) = p_{\text{max}} \sqrt{(i - x_{\text{dim}})^2 + (j - y_{\text{dim}})^2} \]  

Equation 3.3

where \( i \) and \( j \) define the element within the empty IMI array.

Now, for each point within the empty IMI array, the subset of the TOF matrix is searched for the point with angle \( (\beta \text{ not } B) \) and momentum \( p \). The corresponding ion
signal strength is then placed into the empty IMI array. This process is repeated for each point in the IMI array.

An example of an O⁺ IMI plot is shown in figure 3.9, along with a magnified portion, illustrating the Cartesian nature of the underlying grid.

3.7.4 Application of the finite angle correction

The finite angle correction effectively removes the variation of detector acceptance or transmission with ion momentum, as discussed in section 2.4.4.2. This correction is performed in a number of stages. Firstly, the maximum acceptance angle \( \alpha \) for an ion of momentum \( p \), charge \( q \) and mass \( m \) is calculated. This is performed by calculating the passage of ions through the TOFMS. The geometry and electric fields applied to the various elements within the TOFMS are known, and are represented as follows.

If \( s_x \) and \( s_y \) are the displacements of the ion with respect to the source region parallel and perpendicular to the TOFMS axis, the ion travels through three regions:

\[
\begin{align*}
  s_x &\leq s_1 & \text{Equation 3.4} \\
  s_1 &\leq s_x &\leq s_1 + s_2 & \text{Equation 3.5} \\
  s_1 + s_2 &\leq s_x &\leq s_1 + s_2 + s_3 & \text{Equation 3.6}
\end{align*}
\]

where \( s_1 \), \( s_2 \) and \( s_3 \) are the separations between source and top grid, top grid and acceleration grid and acceleration grid and the end of the drift tube in metres. The acceleration of the ion in these regions is governed by the applied electric field. Parallel to the TOFMS axis, the accelerations \( a_{x1} \) and \( a_{x2} \) (in regions 1 and 2 respectively) are given by:

\[
\begin{align*}
  a_{x1} &= \frac{q\varepsilon_1}{m} & \text{Equation 3.7} \\
  a_{x2} &= \frac{q\varepsilon_2}{m} & \text{Equation 3.8}
\end{align*}
\]

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the field strengths in Vm\(^{-1}\). There is no acceleration in region 3 (the drift tube), as the top and bottom of the region are at the same potential.

The initial velocity \( u \) of the ion in the x-direction is given by:

\[
  u_x = \frac{|p| \cos \alpha}{m} & \text{Equation 3.9}
\]

where \( |p| \) is the magnitude of the momentum in amu ms\(^{-1}\), and \( \alpha \) is as before.
Similarly, the initial velocity in the y direction is given by:

\[ u_y = \frac{|p| \sin \alpha}{m} \quad \text{Equation 3.10} \]

There is no variation in the applied electric field perpendicular to the TOFMS axis, hence there isn't any acceleration. Therefore, the distance \( d \) (in metres) that the ion travels perpendicular to the detector given by:

\[ d = u_y t \quad \text{Equation 3.11} \]

where \( t \) is the total flight time in seconds, given by:

\[ t = t_1 + t_2 + t_3 \quad \text{Equation 3.12} \]

where \( t_1, t_2 \) and \( t_3 \) are the flight times through the three regions. To calculate these times, we define

\[ v_{x1} = \sqrt{u_x^2 + 2a_{x1}s_1} \quad \text{Equation 3.13} \]

where \( v_{x1} \) is the velocity of the ion at the end of region 1 \((s = s_1)\). This leads to

\[ v_{x2} = \sqrt{v_{x1}^2 + 2a_{x2}s_2} \quad \text{Equation 3.14} \]

where \( v_{x2} \) is the velocity of the ion at the end of region 2 \((s = s_1 + s_2)\). This allows us to define

\[ t_1 = \frac{v_{x1} - u_x}{a_{x1}} \quad \text{Equation 3.15} \]

\[ t_2 = \frac{v_{x2} - v_{x1}}{a_{x2}} \quad \text{Equation 3.16} \]

\[ t_3 = \frac{s_3}{v_{x2}} \quad \text{Equation 3.17} \]

The distance at which the ion strikes the detector, \( x \) is then calculated for all angles between the momentum vector and the TOFMS axis, referred to as \( \alpha \). If \( x > 1.5 \text{ mm} \), then the ion does not reach the detector, hence defining the maximum angular acceptance for that momentum. This process is illustrated in figure 3.10 for an \( O^{2+} \) ion with initial momentum \( p = 3 \times 10^5 \text{ amu ms}^{-1} \).

The vertical dashed and dotted lines in figure 3.10 represents the top and acceleration grids respectively (see figure 2.2). The ion trajectories in these regions are quadratic with distance along the TOFMS axis. In the drift region, there is no field, hence the trajectories are linear. As can be seen from figure 3.10, if the initial angle \( \alpha \) is greater than 5.5\(^\circ\), the ion strikes the detector outside the aperture. The maximum angle an
The variation of this angle with momentum is shown in figure 3.11.

The final stage of the correction process is to consider all the ions that may contribute to the ion signal $I$ with apparent momentum $p$. If we consider ions generated with momentum $p'$, where $p = |p'| / \cos \alpha$, and angle $\alpha$ is now an arbitrary angle with respect to the TOFMS axis, the TOFMS will resolve these ions as if they
were generated with momentum $p$ at an angle $\alpha = 0^\circ$. However, if the real angle $\alpha$ at which these ions is generated is greater than the angular acceptance $\alpha_{\text{MAX}}$ for momentum $|p'|/\cos\alpha$, the ion cannot reach the detector. To quantify this effect, we calculate the corrected angular acceptance $\alpha^C_{\text{MAX}}$ using the following method.

1. For momentum $p$ and angle $\alpha = 0^\circ$, calculate $\alpha_{\text{MAX}}$ by interpolating the data set similar to that presented in figure 3.11.

2. Increase $\alpha$ by some small quantity (typically 1/20°), calculate $p'/\cos\alpha$, and calculate $\alpha_{\text{MAX}}$ for this angle, again using figure 3.11.

3. If $\alpha$ is greater than $\alpha_{\text{MAX}}$ for the corresponding momentum $p'/\cos\alpha$, this $\alpha$ then becomes $\alpha^C_{\text{MAX}}$. If not, repeat step 2 until this is true.

This process is repeated over the whole range of momenta, giving $\alpha^C_{\text{MAX}}$ as a function of $p$. The correction factor $C$ is then calculated for all momenta using the following expression:

$$C(p) = q \sin^2 \alpha^C_{\text{MAX}}(p)$$  \hspace{1cm} \text{Equation 3.18}

The mechanics of this calculation have been discussed in section 2.4.4.2. Figure 3.12 shows the variation of the correction factor $C$ with $p$ for the $O^{2+}$ ion in an extraction field of 300 V cm$^{-1}$.

Figure 3.12. Variation of the Correction factor $C$ derived from the finite angle correction for an $O^{2+}$ ion.
To complete the correction process, the ion signal I at momentum p is multiplied by the correction factor C at that momentum.

3.7.5 Generating corrected IMI maps
The finite angle correction is applied to the Cartesian array referred to as the raw IMI array. The resulting Cartesian array is referred to as the corrected IMI array. Following this correction, a corrected IMI map is generated in the same manner as in section 3.7.3 by displaying the corrected IMI array as a three-dimensional polar plot.

3.7.6 Data preparation for least-squares fitting
In the following sections, the Monte Carlo simulation technique will be discussed in detail. The result of this process is a two-dimensional Cartesian array, equivalent to the corrected IMI array. To make a comparison between the corrected experimental and simulated results, the simulation is set-up so that both arrays are directly comparable, hence the angle and momentum increments are set to agree with the experimental conditions.

3.8 Monte Carlo simulation of Coulomb explosion
The term 'Monte Carlo' is applied to statistical simulation methods which utilise a series of random numbers to perform the simulation. The predominant reason for using a Monte Carlo technique is that the physical laws governing a particular mathematical or physical system need not be known. Rather, the system is simulated directly. To apply a Monte Carlo technique to a system, the only requirement is that the system can be described by one or more probability density functions. The system is then described by generating random variates by sampling these probability density functions.

3.8.1 Definition of the probability density function (p.d.f.)
Probability density functions are defined in terms of random variates. A random variable is defined as a real number x, which is associated with an event E, where the event E occurs with probability p. However, it is necessary to use continuous random variables, as the geometry of the molecule cannot be described discretely. The probability density function (p.d.f.) \( f(x) \) is defined as the probability \( P \) that the random variable \( x \) is in the interval \( (x, x+dx) \). This is represented in equation 3.19
below.

\[ P(x \leq x_i \leq x + dx) = f(x)dx \]  
Equation 3.19

A p.d.f. can also be described by the probability \( P \) of finding the random variable \( x_i \) in the finite interval \([a, b]\), as shown in equation 3.20.

\[ P(a \leq x \leq b) = \int_a^b f(x)dx \]  
Equation 3.20

There are a number of restrictions that must be applied to generate a valid p.d.f. These conditions are summarised in equations 3.21 and 3.22.

\[ f(x) \geq 0, \quad -\infty < x < \infty \]  
Equation 3.21

\[ \int_{-\infty}^{\infty} f(x)dx = 1 \]  
Equation 3.22

A useful p.d.f. is the uniform function \( U \), defined as follows:

\[ f_U(u) = \begin{cases} 
1, & 0 \leq u \leq 1 \\
0, & \text{otherwise} 
\end{cases} \]  
Equation 3.23

3.8.2 Definition of the cumulative probability distribution function (c.d.f.)

The cumulative distribution function (c.d.f.) \( F_X(x) \) gives the probability that the random variable \( x_i \) is less than or equal to \( x \), as shown in equation 3.24.

\[ P(x \leq x_i) = F_X(x) = \int_{-\infty}^{x} f(x)dx \]  
Equation 3.24

Because of the restrictions applied to \( f(x) \) as described in equations 3.19 and 3.20, \( F_X(x) \) obeys the following conditions.

\[ F_X(x_b) \geq F_X(x_a), \text{ where } a < b \]  
Equation 3.25

\[ F_X(-\infty) = 0 \]  
Equation 3.26

\[ F_X(+\infty) = 1 \]  
Equation 3.27

An example of a Gaussian p.d.f. and the resulting c.d.f. is shown in figure 3.13(a) as generated by the VI shown in figure 3.1. The resulting c.d.f. is shown in figure 3.13(b).

3.8.3 Sampling a p.d.f. using the Inverse Transform method

Let \( X \) be a random variable with c.d.f. \( F_X(x) \). Since \( F_X(x) \) is non-decreasing (see equations 3.25 to 3.27), the inverse function \( F_X^{-1}(y) \) may be defined for any value of
y between 0 and 1. It may be shown that if U (see equation 3.23) is uniformly distributed over the interval (0,1), then

\[ X = F_X^{-1}(U) \]  

Equation 3.28

has the cumulative distribution function \( F_X(x) \). So to generate a value \( x \) of a random variable \( X \), generate a value \( u \) of the random variable \( U \), then calculate \( x = F_X^{-1}(u) \). This process is illustrated in figure 3.14. Compare figure 3.14(b) with figure 3.13(a).

Clearly, to be able to use the Inverse transform method it is necessary to integrate the original p.d.f. to generate the cumulative distribution function. Two methods can be used to perform this integration. Firstly, the integration can be performed analytically, where the p.d.f. is integrated beforehand, and the transform applied accordingly. Distributions to which this method may be applied include exponential, uniform and linear. However, in many cases, it is impossible or very difficult to calculate the integral of a particular function. In this case the second method can be used, in which the integration is carried out numerically. A series of sequential \( x \) values are generated, separated by \( \Delta x \). These values are then used as input into the p.d.f. \( f(x) \). The resulting function is then integrated to generate the c.d.f. \( F_X(x) \). The Inverse transform is then performed via this function. The first method is computationally quicker, as the integration has been performed and the inversion is straightforward.
3.8.4 Application of Monte Carlo methods to laser-induced Coulomb explosion

The Coulomb explosion of molecules has been simulated for a number of molecules using a Monte Carlo method. In this simulation method, the molecule is treated as three atoms, where each atom is ionised according to the channel of interest. The starting positions of each of the ions is defined according to a bend angle ($\theta$), bond length ($r$) and alignment parameter ($\phi$). The definitions of these co-ordinates is illustrated in figure 3.15.
In the present work, the molecule is symmetric, i.e. the two bond lengths are equal. However, to distinguish between each of the bonds, the parameters $r_{12}$ (between ions 1 and 2) and $r_{23}$ (between ions 2 and 3) are defined.

Three probability density functions are used to generate values of the three molecular co-ordinates. These shall be referred to as the $r$-, $\theta$- and $\phi$-distributions. For each simulation, a random variable is generated from each of the p.d.f.'s using the inverse transform method. The atomic ions $I_1$, $I_2$, $I_3$, with charges $q_1$, $q_2$, $q_3$ and masses $m_1$, $m_2$, $m_3$ respectively, are then placed at the positions generated by sampling the p.d.f.'s, then the 'molecule' is allowed to Coulomb explode. The mass and charge of each ion is defined in atomic units.

The explosion is generated by calculating the evolution of the molecule over time under the influence of the Coulomb repulsion. The explosion of the molecule starts at time $t = 0$. The position of each of the ions is calculated in Cartesian space using the following expressions:

\[
\begin{align*}
x_1 &= r_{12} \sin \left( \frac{\theta}{2} \right) \\
y_1 &= -r_{12} \cos \left( \frac{\theta}{2} \right) \\
x_2 &= 0 \\
y_2 &= 0 \\
x_3 &= -r_{23} \cos \left( \frac{\theta}{2} \right) \\
y_3 &= -r_{23} \sin \left( \frac{\theta}{2} \right)
\end{align*}
\]

Equations 3.29(a) - 3.29(f)

where $r$ and $\theta$ are generated from the $r$- and $\theta$-distributions. These co-ordinates are illustrated in figure 3.16.

![Figure 3.16. Conversion from the molecular geometry parameters $r$ and $\theta$ to Cartesian co-ordinates.](image)
At \( t = 0 \), each ion has an initial velocity \( u = 0 \). The velocity of each ion is resolved in the \( x \)- and \( y \)- directions: each of the ions has an associated pair of initial velocity variables \( u_{(1,2,3)X} \) and \( u_{(1,2,3)Y} \).

The force \( F \) between each pair of ions is then calculated using the following series of expressions. Ions 1 and 2 are used as an example, where the parameter \( F_{12x} \) is the component of force between ions 1 and 2 in the \( x \) direction. The expressions for the force between ions 1 and 3 and ions 2 and 3 are similar.

\[
F_{12x} = \frac{14.37q_1q_2(x_1 - x_2)}{[(x_1 - x_2)^2 + (y_1 - y_2)^2]^{3/2}} \quad \text{Equation 3.30(a)}
\]

\[
F_{12y} = \frac{14.37q_1q_2(y_1 - y_2)}{[(x_1 - x_2)^2 + (y_1 - y_2)^2]^{3/2}} \quad \text{Equation 3.30(b)}
\]

Newton's second law \( F = ma \) is then used to calculate the acceleration \( a \) of each ion, again, resolved in the \( x \)- and \( y \)- directions. The following expressions apply to ion 1; similar expressions apply to ions 2 and 3.

\[
a_{1x} = \frac{F_{12x} + F_{13x}}{m_1} \quad \text{Equation 3.31(a)}
\]

\[
a_{1y} = \frac{F_{12y} + F_{13y}}{m_1} \quad \text{Equation 3.31(b)}
\]

Each ion is then allowed to accelerate from initial velocity \( u \) to final velocity \( v \) in time element \( dt \), where the magnitude of the elapsed time \( t \) governs the size of the time element according to the following expressions.

\[
0 \leq t < 0.1, \ dt = 0.02 \quad \text{Equation 3.32(a)}
\]
\[
0.1 \leq t < 1, \ dt = 0.04 \quad \text{Equation 3.32(b)}
\]
\[
1 \leq t < 5, \ dt = 0.1 \quad \text{Equation 3.32(c)}
\]
\[
5 \leq t < 100, \ dt = 0.5 \quad \text{Equation 3.32(d)}
\]
\[
100 \leq t < 10000, \ dt = 1 \quad \text{Equation 3.32(e)}
\]

The expression \( v = u + at \) is used to calculate the final velocity \( v \). When applied to ion 1, the following expressions apply.

\[
v_{1x} = u_{1x} + a_{1x}dt \quad \text{Equation 3.33(a)}
\]
\[
v_{1y} = u_{1y} + a_{1y}dt \quad \text{Equation 3.33(b)}
\]

The change in position \( s \) of each of the ions is calculated using \( s = ut + \frac{1}{2}at^2 \).

\[
s_{1x} = u_{1x}dt + \frac{a_{1x}(dt)^2}{2} \quad \text{Equation 3.34(a)}
\]
The new position of each ion is calculated thus:

\[ x_1' = x_1 + s_{1x} \text{ Equation 3.35(a)} \]

\[ y_1' = y_1 + s_{1y} \text{ Equation 3.35(b)} \]

The elapsed time is now updated to \( t' = t + dt \). The process is repeated from equation 3.30. When \( t = 10000 \), the magnitude of the momentum vector \( |p_{(1,2,3)}| \) and the angle of this momentum vector with respect to the x-axis \( \omega_{(1,2,3)} \) are calculated using the final velocities \( v_{(1,2,3)x} \) and \( v_{(1,2,3)y} \) in the following manner.

\[ |p_1| = 9822.6m_1\sqrt{v_{1x}^2 + v_{1y}^2} \text{ Equation 3.36} \]

\[ \omega_1 = \tan^{-1}\left(\frac{v_{1x}}{v_{1y}}\right) \text{ Equation 3.37} \]

The \( \phi \)-distribution is then sampled to generate the alignment parameter \( \phi \). The uniform function \( U \) is used to generate a random number \( u \), in the interval \((0,1)\). The alignment of the molecule is then simulated by modifying \( \omega_{(1,2,3)} \) according to the following expression.

\[ \omega_{(1,2,3)}' = \omega_{(1,2,3)} + \phi \text{ when } u > 0.5 \text{ Equation 3.38(a)} \]

\[ \omega_{(1,2,3)}' = \omega_{(1,2,3)} - \phi \text{ when } u < 0.5 \text{ Equation 3.38(b)} \]

The output of \( N \) simulations is stored as a \((3 \times N)\) momentum array and a \((3 \times N)\) angle array.

### 3.8.5 Selecting a p.d.f. for Coulomb explosion simulation

When selecting a p.d.f. for the Coulomb explosion simulation, a number of factors are taken into account. These criteria are summarised below.

1. Sampling the p.d.f. using the inverse transform method should be computationally efficient.
2. Has the p.d.f. been applied to Coulomb explosion previously?
3. Is the p.d.f. physically reasonable?

The first criterion depends on whether the c.d.f. can be generated analytically (i.e. before the simulation process starts) or whether it has to be calculated numerically. As discussed in section 3.8.4, the former is preferable, as processing time is minimised. Functions of this form include linear, quadratic, simple trigonometric and...
simple exponential forms.

Addressing the second criterion, Cornaggia (1996) used a Monte Carlo technique employing symmetric triangular distributions to represent the r, θ and φ distributions. Therefore, to make this analysis comparable with the work of Cornaggia (1996), using triangular distributions would be beneficial. Furthermore, triangular p.d.f.'s may be integrated easily, hence fulfilling the first criteria.

The third criterion is more difficult to meet, as the form of the laser-influenced r and θ distributions are unknown. However, it is fair to say that any p.d.f. for the r distribution should meet the following criteria:

a) The p.d.f. should start from \( f(r) = 0 \) at some value of \( r \) (\( r_1 \) say).

b) The p.d.f. should rise to a peak at some value of \( r \) (\( r_2 \), where \( r_2 > r_1 \)).

c) The p.d.f. should return to \( f(r) = 0 \) at some value of \( r \) (\( r_3 \), where \( r_3 > r_2 \)).

In the case of the θ distribution, the (c) criteria doesn't necessarily apply - it is possible that the θ distribution could have some non-zero value around θ = 180 degrees.

The natural choice for a p.d.f. to represent this type of physical situation would be a Gaussian form. However, it was decided that three triangular distributions would be used to represent the bend-angle and bond-length p.d.f.'s. Clearly, triangular distributions meet criteria 1 and 2. A compromise is made in the case of criterion 3. Furthermore, using a Gaussian distribution has the disadvantage that the p.d.f. is always symmetric. It would be advantageous to be able to allow the bond-length distribution to be asymmetric.

In the case of the φ distribution, it is assumed that the laser-induced reorientation is strongest along the laser polarisation direction. Another triangular distribution is used to represent the φ distribution, with a maximum at zero degrees, and falling to zero symmetrically around the peak.

### 3.8.6 Generating the Coulomb explosion c.d.f.'s

The triangular p.d.f.'s are defined by a number of parameters, which define the position of the peak of the distribution and the point(s) at which the p.d.f. falls to zero. The three triangular distributions are represented as shown in figure 3.17. The labels 1-8 in figure 3.17 are defined as shown in table 3.1 below.
To allow sampling of these p.d.f.'s using the inverse transform method, it is necessary to generate the cumulative distribution function.

Figure 3.18(a) shows a triangular p.d.f. similar to those defined in figure 3.17. The corresponding c.d.f is shown in figure 3.18(b). As can be seen, the c.d.f. takes the form of two parabolas (shown in blue and red), clearly due to integrating the linear...
Figure 3.18. (a) An example triangular p.d.f. and (b) corresponding c.d.f.

Form of the triangular p.d.f. The result of applying the inverse transform method is shown in figure 3.19.

Figure 3.19. (a) Sampling the triangular c.d.f. using the Uniform distribution. (b) Resulting distribution of samples.

This is the type of distribution used to represent the geometry of the molecules studied in the present work.
3.8.7 Example Monte Carlo Coulomb explosion simulation.
To demonstrate the Monte Carlo technique, a test molecule, ozone (O₃), is simulated under 'realistic' geometry distributions. The bond length distribution is chosen to be $r_{pk} = 2r_e$, $r_{\text{min}} = r_e$ and $r_{\text{max}} = 3r_e$ where $r_e = 1.28$ Å. The bend angle distribution is chosen with $\theta_{pk} = 117^\circ$, $\theta_{\text{min}} = 97^\circ$ and $\theta_{\text{max}} = 137^\circ$. The alignment distribution was set as $\varphi_{\text{wid}} = 40$. Note that this simulation assumes one of the O-O axes aligns with the laser polarization direction. If the molecule is triply ionized, Coulomb explosion into the (1,1,1) channels likely. Two of the three O⁺ ions will be ejected around the polarization direction, and the third will be ejected perpendicular. These two processes are illustrated in figure 3.20(a) and (b) respectively.

![Monte Carlo simulation of the Coulomb explosion of triply-ionized ozone. (a) O⁺ ions ejected along the polarization direction. (b) O⁺ ions ejected perpendicular to the polarization direction.](image_url)
Chapter 4. Geometry modification and reorientation of H₂O investigated using ion-momentum imaging

4.1 Introduction

This chapter will describe experimental investigations of laser-induced reorientation and geometry modification in water. Experimental methods and data processing techniques described in chapters 2 and 3 will be employed to examine how the H₂O molecule Coulomb explodes in 790 nm 50 fs laser pulses. The Monte Carlo technique described in chapter 3 will then be used to quantify the geometry of the exploding molecule. Finally, the implications of the simulated results will be analysed in terms of light-dressed potentials.

The laser parameters used throughout this chapter are summarised in table 4.1.

<table>
<thead>
<tr>
<th>Laser parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>790 nm</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>55 fs</td>
</tr>
<tr>
<td>Pulse energy</td>
<td>0.9 mJ</td>
</tr>
<tr>
<td>Beam diameter</td>
<td>1 cm</td>
</tr>
<tr>
<td>Focussing</td>
<td>65 spherical mirror</td>
</tr>
<tr>
<td>Peak intensity</td>
<td>3 × 10¹⁴ Wcm⁻²</td>
</tr>
</tbody>
</table>

4.2 Preparation of H₂O target

The ampoule in the gas line (see chapter 2, figure 2.4) was filled with de-ionized water, lightly heated under vacuum, causing impurities in the sample liquid to pass into the backing line. Following outgasing, the gas line is evacuated to 1 × 10⁻³ Torr and the on/off valve to the ampoule opened, filling the gas line with ultra-pure H₂O. The UHV needle valve on the top of the spectrometer (see figure 2.1) was then opened, allowing the target gas into the interaction region. The chamber was filled to a background pressure of 1 × 10⁻⁷ Torr.

Laser pulses are then allowed into the TOFMS, and a TOF spectrum recorded with the laser polarization parallel to the spectrometer axis. This is shown in figure 4.1. The peaks in the TOF spectrum were identified using the technique detailed in section 2.4.1.

Figure 4.2 shows the section of the TOF spectrum containing the H⁺ ion, illustrating the origin of the different peaks. As in earlier chapters, the notation (1,1,1) corresponds to the Coulomb channel H₂O³⁺ → H⁺ + O⁺ + H⁺. In addition, the
Figure 4.1 Time-of-flight spectrum of H₂O recorded with 50 fs laser pulses at an intensity of 3 × 10¹⁶ Wcm⁻². The laser polarization direction is parallel to the TOFMS axis.

Figure 4.2 H⁺ ions from the laser-H₂O interaction, with the laser parameters as in figure 4.1. Channels (1,0,1) and (1,0) correspond to the H₂O²⁺ → H⁺ + O + H⁺ and H₂O⁺ → H⁺ + OH decay pathways respectively. These channel assignments were made following
calculations of the expected kinetic energy release (KER) for all of the above
canals. The (1,1) channel is also present, generating a KER = 7.6 eV. However,
comparing the ratios of the O$^+$ and O$^{2+}$ ions to the OH$^+$ ion, it is clear that this
channel is weak.

4.3 TOF matrix of $\text{H}_2\text{O}$

Following the identification of the ions in the TOF spectrum, a TOF matrix was
recorded for $\text{H}_2\text{O}$. The laser polarization was rotated and a 100-shot average TOF
spectrum recorded every 2°. Following rotation of the polarization through 360°, a
TOF matrix (see section 3.7.2) was constructed. The TOF matrix for $\text{H}_2\text{O}$ is shown
in figure 4.3.

A number of observations may be made from figure 4.3. Firstly, the H$^+$ ion signal is
strongly anisotropic, with the maxima parallel to the axis of the TOFMS. Following
experimental observations leading to the idea of laser-induced reorientation (see
section 1.6), it would appear that the H-H axis of the molecule is strongly aligned
with the laser polarization direction.

![Figure 4.3. TOF matrix of $\text{H}_2\text{O}$. The angle $\beta$ is the angle between the TOFMS axis and the laser polarization direction.](image-url)
Secondly, there appears to be a broadening of the oxygen ion signal, which is maximised perpendicular to the TOFMS axis. The oxygen fragments are peaked at zero momentum, indicating that the ions are released from a near-linear geometry. This preliminary conclusion is drawn before data correction and will be returned to later.

4.4 Uncorrected H$_2$O IMI maps

To further understand the Coulomb explosion of H$_2$O, it is necessary to convert the TOF matrix into IMI maps. This process was described in detail in section 3.7.3. After identifying the zero-momentum time-of-flight for the H$^+$, O$^+$ and O$^{2+}$ ions, IMI maps are generated from the relevant section of the TOF matrix. These are shown in figure 4.4(a)-(c). The vertical axis is parallel to the laser polarization direction. Clear information can be gained from these plots. Figure 4.4(a) shows a low-momentum island (<10 x 10$^3$ amu ms$^{-1}$) consisting of ions from the H$^+$ + OH (1,0) channel, as identified in figure 4.3. The island is nearly circular, indicating that the angular distribution of these ions is nearly isotropic. This area of the momentum map is presented in figure 4.5. The crescent-shaped islands, which consist of ions from the Coulomb channels (1,1,1) and (1,2,1), have a wide angular distribution, but are not isotropic. The colour scale shows that these islands peak around 0° and 180°, which indicates that the Coulomb explosions result from H$_2$O molecules in which a certain amount of alignment exists between the H-H axis and the laser polarization direction. We have fitted a function of the form Acos$^n$θ to the H$^+$ angular distribution, at a momentum of 40 x 10$^3$ amu ms$^{-1}$, which is close to the highest point on the island at 0° and 180°. The least-squares fit gives a value of n = 4.5, which compares with n = 12 for the (1,1,1) channel of CO$_2$ at the same laser intensity (see Sanderson et al 1998b, in Appendix A8.6). We can try to explain the observations of both the low- and high-momentum hydrogen fragments by considering a number of important results.

Recent experiments with laser pulses of less than 100 fs and intensity greater than 10$^{14}$ Wcm$^{-2}$ (Ellert et al 1998, Posthumus et al 1998, as discussed in section 1.5.1) have shown that light diatomic molecules are reorientated by the laser field. By contrast it was found that the massive I$_2$ molecule could not be reoriented on such a short time scale. The H$_2$O molecule is light and so it is reasonable to assume that the
Figure 4.4. Momentum maps for the atomic fragment ions resulting from the Coulomb explosion of H$_2$O. The arrow shows the direction of the laser polarization direction.
origin of the angular distribution, observed here, is the reorientation of the molecule by the laser field. Bhardwaj et al (1997) measured the fragment ions resulting from the interaction of 30 ps laser pulses with water at an intensity of $10^{13}$ Wcm$^{-2}$. The angular distributions of H$^+$ ions, most probably from the (1,0) channel, were measured and found to be isotropic. This observation is confirmed in the present work, as the low-momentum H$^+$ ions must originate from a region within the focal spot where the intensity is low enough to result in only single ionization channels such as (1,0). Bhardwaj et al (1997) also calculated the static field-induced dipole strengths parallel and perpendicular to the H-H axis, and showed that at higher intensities, the parallel-induced dipole dominates, hence the molecule should be rotated, such that the H-H axis aligns with the laser field. This prediction is confirmed by the present result.

The effect of opposing torques should reduce the amount of reorientation experienced by the molecule in comparison with more linear molecules such as CO$_2$, leading to a lower value of $n$ as observed here. Furthermore, the bent nature of H$_2$O is important in widening the angular distribution of the Coulomb channel in a very simple way. If the H-H axis is completely aligned with the polarization direction, the trajectories of the H$^+$ ions cannot be along the polarization direction, because of the repulsion from the laterally offset oxygen ion. The bent nature of H$_2$O is deducible from Figs. 4.4 (b) and (c) in which the O$^-$ and O$^{2+}$ momentum plots are elliptical. In both cases the major axis of the ellipse is orientated at 90° to the laser polarization direction. This indicates that the molecules aligned with the H-H axis along the

Figure 4.5. Expanded area of the H$^+$ momentum map, showing the (1,0) channel in the centre.
polarization direction repel the central oxygen ion at right angles to the polarization direction; this is only possible from a bent geometry, as discussed in section 1.6.2.

4.5 Corrected H$_2$O IMI maps
Further information about the molecular geometry can be extracted from the momentum maps, but first it is necessary to correct the data for the effect of the variation of detector acceptance angle with ion momentum. This variation has the most effect on the oxygen ion maps in Figs. 4.4 (b) and (c), because the momenta of the oxygen fragments are small, and so the acceptance angle becomes large, reaching 90° for momenta close to zero. This means that the ion distributions appear more isotropic than is physically the case. The correction procedure was discussed in section 3.7.4, hence only the results of applying the correction will be presented.

Figures 4.6 (a)-(c) show the angular distributions of H$^+$, O$^+$, and O$^{2+}$ respectively, after a correction for the variation of acceptance angle. In Fig. 4.6 (a) the central island is now not visible, but the Coulomb islands have not been greatly altered, as their momentum is high. The major difference is in Figs. 4.6 (b) and (c) where removing the false isotropy has transformed the elliptical islands into bow-tie shaped islands. It is now possible to use the three corrected maps to deduce the geometry of the exploding molecule, by comparing them with maps derived from a Monte Carlo simulation of the Coulomb explosion of the H$_2$O molecule from a distribution of geometries.

4.6 Monte Carlo simulation of the Coulomb explosion of H$_2$O
The simulation technique used to analyse the Coulomb explosion of H$_2$O has been discussed in chapter 3 hence minimal detail will be presented here. Three independent distributions are chosen to represent the O-H bond length $r$, the H-O-H bond angle $\theta$, and the alignment angle $\phi$ between the H-H axis and the laser polarization direction. The distributions used are either triangles or trapeziums for ease of calculation, as discussed in chapter 3.

To simplify the simulation process further, we consider only the three-body Coulomb explosion channels. When the H$_2$O molecule is ionized three or four times, the resulting ion (H$_2$O$^{3+}$ or H$_2$O$^{4+}$) Coulomb explodes into either the (1,1,1) or (1,2,1) channel, where the channel assignment is H$_2$O$^{(n+2)+} \rightarrow$ H$^+$ + O$^{n+}$ + H$^+$. 
Figure 4.6. Momentum maps for the atomic fragment ions resulting from the Coulomb explosion of H$_2$O. The ion signal has been corrected for detector acceptance using the method described in chapter 2.
Because of the considerable difference between the signal strength and the H$^+$ momentum of the (1,0) and (1,0,1) dissociative channels and the (1,1,1) and (1,2,1) three-body Coulomb channels, the dissociative channels will be ignored.

The first step of the simulation process was to apply three conditions that were ascertained from the corrected IMI maps as shown in figure 4.6. These conditions are:

1. A critical distance of double the ground state equilibrium separation ($r_e = 0.96 \text{ Å}$) was assumed, in accordance with the majority of earlier experimental evidence (see section 1.4,1). The critical distance was rounded to 2 Å for ease of computation. The $r$-distribution used had a full-width at base of ±1 Å.

2. It was initially assumed that the molecule was exploding from around the equilibrium bend angle ($\theta = 104.5^\circ$). The width of the bend angle distribution was estimated from the potential energy surface for the ground state of H$_2$O as published by Schneider et al (1996), and was defined as ±7°.

3. The width of the alignment distribution was estimated by measuring the full-width half maximum of the H$^+$ ions at \(40 \times 10^3\) amu ms$^{-1}$, which gave FWHM of 60°. This is approximated by a triangular $\phi$-distribution with a full-width at base of 60°.

An initial test for these assumptions was performed by setting the bond length and bend angle in the "calculate momenta and angles.vi" subVI of the Monte Carlo software, which calculates the final ion momenta for a certain geometry. The result of this simulation for the (1,1,1) channel is shown in figure 4.7.

Comparing the results of this simulation with the corrected IMI maps for H$^+$ and O$^+$ (figures 4.6(a) and (b) respectively), it can be seen that these results are within the limits of the data.

Using the simulation parameters outlined above, the Coulomb explosion of H$_2$O was simulated for the (1,1,1) and (1,2,1) channels. The results of a 3500 iteration run are shown in figure 4.8. The simulation parameters are shown in figure 4.9.

Comparing figures 4.6 and 4.8, a number of similarities and striking differences can be seen. In the case of the hydrogen ions, the following observations have been made:

- Both the angular width and the momentum width of the simulated H$^+$ from the (1,1,1) channel (see figure 4.8(a)) compare rather unfavorably with the measured
H+ distribution (see figure 4.6(a)).

- There is reasonable agreement between the width of the momentum distribution along the laser axis and the position of the peak momentum of the simulated H+ ion from the (1,2,1) channel (see figure 4.8(b)) as compared to the measured H+ (see figure 4.6(a)).

- The width of the angular distribution of the simulated H+ ions from the (1,2,1) channel is considerably wider than the observed H+ distribution.

In the case of the oxygen ions, the following observations have been made:

- The width of the momentum distributions of both the simulated O+ and O2+ ions (see figures 4.8(c) and (d)) are far narrower than the measured distributions (see figures 4.6(b) and (c)).

- For both the simulated O+ and O2+ ions (see figures 4.8(c) and (d)), the peak in the momentum distribution is observed to lie at a far higher momentum as compared to the measured results (see figures 4.6(b) and (c)).

- Again, in the case of both the simulated O+ and O2+ ions (see figures 4.8(c) and (d)), the width of the angular distributions is observed to be considerably higher than the measured results (see figures 4.6(b) and (c)).
Importantly, the absolute value of the momentum of the hydrogen ions is of the right order, hence it would appear that Coulomb explosion from around double the equilibrium separation is correct. However, the differences between the corrected experimental (figure 4.6) and simulated IMI data (figure 4.8) indicates that some of the initial assumptions listed above are wrong. The angular distribution of the simulated hydrogen ions is wider than the experimental results, hence there is a problem with either the \( \theta \)- or \( \phi \)-distributions (or a combination of the two).

Turning to the oxygen ions, the observations listed above indicates that too small a range of bends is being included in the simulation. Secondly, the angular width of the oxygen ions is too high, indicating (as with the hydrogen ions) that the combination of the \( \theta \)- and \( \phi \)-distributions has caused excessive broadening.

The arguments given above lead us to conclude that our assumptions about the critical distance are in reasonable agreement with the observed results. However, the molecule cannot be exploding from anywhere near the equilibrium bend angle distribution. To try to improve the agreement between the simulated and measured results, a number of changes were made to the simulation parameters. Two important conditions were applied while adjusting the simulation parameters. Firstly,
only one of the parameters was changed at a time. This allowed us to make reasonable judgements as to the overall effect of the changes made, as changing more than one parameter at a time could create counteracting effects. Secondly, the (1,1,1) and (1,2,1) channels were allowed to have different parameters, as it was felt than constraining the channels to behave in the same manner might be unphysical.

Crucially, this step-by-step approach allowed an insight into the explosion dynamics of the molecule. This insight accelerated the simulation process, as it allowed us to understand how the three geometrical quantities (r, θ and φ) interacted to generate hydrogen and oxygen ions of certain momenta. Vitally, the simulation process was carried out in a 'global' manner, where each parameter change was examined for all ions from both channels.

To aid understanding of the simulation process, the effects of varying each of the parameters individually has been rationalized into a set of diagrams, which are presented below. These diagrams can be thought of as a set of 'rules' for the
simulation, and are included to illustrate how the simulated results were iterated, rather than presenting each step along the way, as in the majority of the cases, the amount of variation is small. The variations in the form of the H⁺ and O⁺ depending on the shape of the alignment, bond length and bend angle distributions are presented in figures 4.10 to 4.13.

The change in form of the O²⁺ ions has not been presented, as the momentum of the ion is proportional to the charge of the ion, hence the effect is the same as with the O⁺, but magnified. In figures 4.10 to 4.13, the original distribution is shown as a dashed line, and the change in the distribution is shown as a solid line. The arrow along the x-axis of the probability distribution in figures 4.10 to 4.13 shows the parameter change. The change in shape of the H⁺ and O⁺ IMI maps is shown schematically. Again, the original shape of the distribution of ions is shown as a dashed line, and the change in shape is shown as a solid line. The arrows show the shift in the shape of the maps. The original shape of the IMI maps was chosen to illustrate the effect, and are qualitative.

Importantly, the effect of altering the distribution can be thought of as reversible, i.e. if a certain parameter is increased and a particular set of change observed, similar but opposite effects will occur if the parameter is varied in the opposite direction. In essence, if the direction of the arrow showing the change in shape of the distribution is reflected about its starting position, the arrows showing the change in form of the IMI maps are also reflected about their starting positions.

The variation of the form of the H⁺ and O⁺ ions with variations in the alignment distribution is presented in figure 4.10. It is assumed that the alignment distribution is peaked around the laser polarization direction, therefore the only parameter that can be varied is the width of the distribution. As can be seen from figure 4.9,

\[ \phi_{\text{max}2} > \phi_{\text{max}1} \]

Figure 4.10. Illustration of the change in shape of the H⁺ and O⁺ IMIs with an increase in the width of the \( \phi \) distribution.
increasing the width of the alignment distribution causes the H⁺ and O⁺ ions to be spread over a larger angular range.

Figure 4.11 illustrates how the H⁺ and O⁺ ions are affected by changes in the bond length distribution. Unlike the alignment distribution, the bond length distribution may be changed in three ways: shifting the entire distribution in r, which is accomplished by leaving the width of the distribution (\( r_{\text{wid}} \)) the same and increasing the peak value (\( r_{\text{pk}} \)), increasing the highest value of r at which the distribution falls to zero (\( r_{\text{max}} \)), and decreasing the lowest value of r at which the distribution falls to zero (\( r_{\text{min}} \)).

The bend angle distribution may be changed in a manner analogous to the bond length distribution. This is illustrated in figure 4.12.

The bend angle distribution is also allowed to 'saturate' at angles \( \theta < 180^\circ \). The term saturate implies that at some angle less than 180°, the distribution does not return to zero. This condition is specific to the bend angle distribution, as it is unphysical for the bond length distribution to not return to zero at high r. The effect of saturating the bend angle distribution is shown in figure 4.13.

Comparing figures 4.11 and 4.12, it can be seen that the changes brought about by
changing the bond length and bend angle distributions are similar. However, there are subtle differences. Looking at the effect of changing the peak position (top of figures 4.11 and 4.12), shifting the bond length distribution to higher \( r \) causes both the \( H^+ \) and \( O^+ \) islands to move towards the centre of the IMI map. However, in the case of the bend angle distribution, the effect on the \( H^+ \) ion is much smaller and the effect on the \( O^+ \) ion is larger.
To successfully reproduce the experimental results, the following series of conditions were applied to the simulation parameters. Note that throughout this fitting procedure, a ratio of 7:10 was maintained between the hydrogen ions from the (1,1,1) and (1,2,1) channels when constructing the simulated hydrogen IMI maps.

- The r-distribution was maintained as in the original simulation, hence $r_{pk} = 2 \text{Å}$, $r_{min} = 1 \text{Å}$ and $r_{max} = 3 \text{Å}$. Shifting the peak of the r-distribution caused the agreement between the experimental and simulated momentum of the hydrogen ions to worsen.

- The $\theta$-distribution was widened to $\pm 20^\circ$ around the peak value $\theta_{pk} = 104.5^\circ$, causing considerable widening of the hydrogen and oxygen ions. This improved the fit for the oxygen ions marginally, without upsetting the hydrogen fit.

- The $\phi$-distribution was narrowed, improving the fit for the hydrogen ions, but making the angular distribution of the oxygen ions far too narrow. As a consequence, the $\phi$-distribution was left as $\phi_{wid} = 60^\circ$.

These conditions lead us to conclude that the molecule could not be exploding from the equilibrium bend angle, hence the more drastic changes below were carried out.

- The peak in the $\theta$-distribution was increased to $130^\circ$. This improved the oxygen ion fit considerably, as there was an increase in ions with low momentum. There was a small decrease in the momentum of the hydrogen ions.

- The width of the r-distribution was increased slightly to $r_{min} = 0.5 \text{Å}$ and $r_{max} = 3.5 \text{Å}$. This improved the fit on the oxygen ions further, and by this point the experimental hydrogen ions are well reproduced by the simulation.

- The $\theta$-distribution was extended out to $\theta_{max} = 180^\circ$. This improved the fit of the low momentum oxygen ions without affecting the hydrogen ions.

- The $\theta$-distribution was allowed to saturate from $130^\circ$ to $180^\circ$, as shown in figure 4.13. This rather dramatic change improved the oxygen ion distributions to the point that only small subsequent changes were deemed necessary.

To conclude the fitting process, a least-squares fit was employed. Slight variations were made in the r, $\theta$ and $\phi$ distributions, and the ratio between the (1,1,1) and (1,2,1) channels was adjusted slightly.

### 4.7 Simulation results

Figures 4.14(a) – (c) show the final best-fit distributions for r, $\theta$, and $\phi$. For both
channels, the \( r \) distribution was found to peak at 2\( \text{Å} \). It was found that the experimental results were best reproduced by an \( r \)-distribution of \( \pm 1.5 \text{ Å} \) (hence \( r_{\text{min}} = 0.5 \text{ Å}, r_{\text{max}} = 3.5 \text{ Å} \)).

The best-fit \( \phi \) distribution narrows with increasing ionization channel as expected. For the (1,1,1) channel, \( \phi_{\text{wid}} = 70^\circ \), narrowing to \( \phi_{\text{wid}} = 60^\circ \) for the (1,2,1) channel. In Sanderson \textit{et al} (1998), triangular alignment distributions with full width at half maximum of 60\(^\circ\) and 40\(^\circ\) were derived to describe the (1,1,1) and (1,2,1) channels of \( \text{CO}_2 \). This implies reorientation of \( \text{H}_2\text{O} \), but to a lesser extent than in \( \text{CO}_2 \), due to competition between the parallel and perpendicular torques. This will be discussed later.

The shape of the best-fit \( r \) and \( \phi \) distributions was expected to some extent, as illustrated by not having to change the distributions much from the original attempt. However, the extent by which the \( \theta \) distribution had to be changed was not expected. In the case of the (1,1,1) channel, \( \theta_{\text{min}} = 70^\circ \), rising to a probability of 1 at \( \theta_{\text{pk}} = 130^\circ \), and remaining at 1 until 180\(^\circ\). The (1,2,1) channel was found to behave similarly, with \( \theta_{\text{min}} = 90^\circ \), rising to 1 at \( \theta_{\text{pk}} = 140^\circ \), again saturated until 180\(^\circ\). This is

![Diagram](image)

**Figure 4.14.** Best-fit simulation parameters found after a number of iterations of the simulation process.
Figure 4.15. Comparison between the best fit simulated and corrected experimental maps resulting from the Coulomb explosion of H$_2$O. (a) The simulated results are shown on the right-hand side of the figure, the experimental on the left. (b) and (c) The simulated results are presented on the bottom half of the plot, the experimental on the top.
dramatically different from the expected distribution, peaked at $\theta_{pk} = 104.5^\circ$ with a full-width half maximum of $\theta_{wh} = 14^\circ$ (as shown in figure 4.9).

Figures 4.15(a) – (c) show a comparison between the corrected experimental maps and the best-fit simulated maps. The general agreement is good, with the simulated maps reproducing the shape of the islands and the positions of the highest ion signal in the experimental maps.

### 4.8 Discussion of results

Following the completion of the simulation process it is necessary to explain the results and understand them with respect to other experimental and theoretical work. This will be discussed in the following sections.

### 4.9 Discussion of results - enhanced ionization

We initially assumed that Coulomb explosion would occur from around double the equilibrium separation, and the best-fit results are consistent with this notion. It is apparent from our results that H$_2$O$^{3+}$ and H$_2$O$^{4+}$ Coulomb explode from a critical separation of $r_c = 2$ Å. These results are consistent with the analysis of Schmidt et al (1994), who found that the following relationship held for a range of molecules:

$$r_c \approx 2.3\sqrt{r_e} \quad \text{Equation 4.1}$$

Where $r_e$ is the equilibrium separation, which in the case of H$_2$O is 0.96 Å. Using this value in equation 4.1, Schmidt et al (1994) predict $r_c = 2.25$ Å. However, Schmidt et al (1994) averaged the constant of proportionality of equation 4.1 over a wide range of molecules. Included in this averaging were the results of Cornaggia et al 1994 who examined the Coulomb explosion of CO$_2$. We choose the constant of proportionality found by Cornaggia et al 1994, which slightly changes equation 4.1 to:

$$r_c = 2.2\sqrt{r_e} \quad \text{Equation 4.2}$$

This gives an estimate of $r_c = 2.16$ Å, in good agreement with our results.

Full quantum mechanical treatments of enhanced ionization in triatomics are somewhat scarce, however Bandrauk and co-workers have examined the process in linear H$_3^+$ and H$_3^{2+}$ and non-linear H$_3^{2+}$. It was found, in the case of the simplest triatomic H$_3^{2+}$ that the critical separation may be approximated by:
where $I_p$ is the ionization potential of the molecule in au, and $r_c$ is also in au. There are differences between the laser conditions in the present work ($\lambda = 800$ nm, $I = 3 \times 10^{16}$ Wcm$^{-2}$, pulse length = 50 fs) and those of Bandrauk and Ruel (1999) ($\lambda = 1064$ nm, $I = 10^{14}$ Wcm$^{-2}$, pulse length = 30 cycles, with 5 cycle linear ramp on), however, the comparison is still worthwhile.

Table 4.2 shows the measured ionization potentials of $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^{n+}$ (where $n=1$ - 3), along with the critical separations as predicted by equation 4.3. The ionization potential of $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+$ (12.662 eV) was taken from Reutt et al (1986), and the ionization potentials of $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^{2+}$ (13.939 eV) and $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^{3+}$ (16.973 eV) are taken from Dutuit et al (1985). As is apparent from table 4.2, and the calculations based on equation 4.2, there is reasonable agreement between the predictions of Bandrauk and Ruel (1999), Schmidt et al (1994) and the present results, implying Coulomb explosion from a critical distance around $r_c = 2\text{Å}$.

**Table 4.2. Critical separation $r_c$ in $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^{n+}$ as predicted by Bandrauk and Ruel (1999)**

<table>
<thead>
<tr>
<th>$n$</th>
<th>$I_p$ (au)</th>
<th>$r_c$ (au)</th>
<th>$r_c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.46</td>
<td>5.43</td>
<td>2.9</td>
</tr>
<tr>
<td>2</td>
<td>0.51</td>
<td>4.90</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>0.62</td>
<td>4.03</td>
<td>2.1</td>
</tr>
</tbody>
</table>

4.10 Discussion of results - laser-induced reorientation of $\text{H}_2\text{O}$

The narrowing of the alignment distribution is an indication that laser induced reorientation is occurring. This observation was expected, given that reorientation has been observed in CO$_2$ (Sanderson et al 1998b for initial observations, next chapter for more detailed treatment). However, we want to quantify the reorientation of $\text{H}_2\text{O}$ in the 50 fs laser pulse. Using a classical model, the reorientation time of $\text{H}_2\text{O}$ may be estimated by treating the molecule as a rigid rotor.

Adapting the treatment of Bandrauk and Ruel (1999), the pendular frequency $\omega_p$ of the $\text{H}_3$ molecule in a linearly polarized laser field is given by:

$$\omega_p = \sqrt{\frac{E_o^2 \alpha}{2M}} \quad \text{Equation 4.4}$$

where $E_o$ is the peak electric field strength, $\alpha$ is the molecular polarizability and $M$ is the moment of inertia, all in au. The symbol $M$ is used for moment of inertia to avoid
confusion with laser intensity $I$. The corresponding period of the reorientation motion $T_{re}$ is then simply given by:

$$T_{re} = \frac{2\pi}{\omega_p} \quad \text{Equation 4.5}$$

Given a random distribution of molecules within the laser focus, the maximum angle between the molecule and the field is $90^\circ$, hence the maximum reorientation time required is a quarter of the period of the reorientation motion. This is referred to as the reorientation time $T_{1/4}$, which is given by:

$$T_{1/4} = \frac{\pi}{2\omega_p} \quad \text{Equation 4.6}$$

The $\text{H}_2\text{O}$ molecule has a polarizability of $\alpha = 1.45 \text{ Å}^3 = 9.79 \text{ au}$. In the present work, the maximum laser intensity is $3 \times 10^{16} \text{ Wcm}^{-2}$, which corresponds to a maximum electric field strength $E_0 = 0.923 \text{ au}$. Through geometrical considerations, the momentum of inertia of the $\text{H}_2\text{O}$ molecule in the equilibrium position ($\theta = 104.5^\circ$, $r = 1.81 \text{ au}$) is $M = 1.2 \times 10^4 \text{ au}$. Substituting these values into equation 4.6, the reorientation time $T_{1/4} = 173 \text{ au} = 2 \text{ fs}$.

If we now include the observation that during the ionization process, the bond length increases from $r_e = 1.81 \text{ au}$ to $r_e = 3.78 \text{ au}$ (a factor of 2.1), there will be an increase in the reorientation time $T_{1/4}$ as the molecular bonds stretch. If we consider that the moment of inertia $M \propto r^2$, we find $T_{1/4} \propto r$, hence if the molecular bonds increase to $r_e = 3.78 \text{ au}$, the reorientation time increases to $T_{1/4} = 4.2 \text{ fs}$.

In the present work, with a laser wavelength of 800 nm, the electric field period is 2.7 fs, hence, in terms of this simple treatment, the molecule will be reorientated on the same time scale as the laser period. However, the reorientation time is only an estimate, given the maximum laser intensity present.

This conclusion is reinforced by the recent theoretical study by Bhardwaj et al. (1997), who calculated the two components of the induced dipole moments for $\text{H}_2\text{O}$ as a function of applied electric field strength. The interaction of the electric field with the permanent and induced dipole moments returns to the original suggestions of Strickland et al. (1992) and Friedrich and Herschbach (1995), which were discussed in chapter 1.
Bhardwaj et al (1997) modelled the electronic structure of the H$_2$O molecule using a static field method, and calculated the distortion of the electron wavefunction, hence allowing the calculation of the induced dipole moments. The results of these calculations are presented in figure 4.16. As can be seen from figure 4.16, at moderate intensities ($I < 3 \times 10^{14}$ Wcm$^{-2}$), the induced moment perpendicular to the H-H axis dominates, hence we would expect the H-H axis to reorientate to lie perpendicular to the laser polarization direction. However, at intensities $I > 3 \times 10^{14}$ Wcm$^{-2}$, the induced moment parallel to the H-H axis begins to dominate the perpendicular moment. Bhardwaj et al (1997) only calculated the induced dipole moments for intensities up to $10^{15}$ Wcm$^{-2}$, shown as points in figure 4.16. However, if we make a linear extrapolation of the behaviour of the parallel moment, it is apparent that at the intensities employed in the present work (far right hand side), that the induced moment perpendicular to the H-H axis will be negligible. We would therefore conclude that the H-H axis of the molecule will reorientate along the laser polarization direction within the rising edge of the laser pulse.
4.11 Discussion of results - bend angle softening of $H_2O$

The maximum in the bond angle ($\theta$) distribution is at 130° for the (1,1,1) channel and 140° for the (1,2,1) channel. This compares with a most probable angle of 104° for the neutral molecule, hence there is a considerable straightening motion involved during the dissociation and Coulomb explosion of the molecule.

Werner et al (1995) experimentally investigated the Coulomb explosion of $H_2O \rightarrow H_2O^{3+}$ and $H_2O^{4+}$ by HCl impact ($H^+ @ 250 \text{ keV}$, $O^{6+} @ 92.4 \text{ keV}$, $O^{7+} @ 126 \text{ keV}$ and 742 keV). They measured the angle $\theta_v$ between the momentum vectors of exploding $H^+$ ions, rather than the bend angle of the molecule. The authors reported that their experimental results were well reproduced by a Monte Carlo simulation based on multiconfiguration self-consistent field (MCSCF) calculations, which took into account a number of states of the exploding ion. Figure 4.17 shows a comparison between the best-fit simulation results from the present work and the calculations of Werner et al (1995).

The distributions of Werner et al (1995) describe the molecular ion geometries well. However, the bend angle distribution cannot be derived directly, as the molecule-HCl reaction was not purely Coulombic. Nevertheless, the dissociation is close to Coulombic, hence the $\theta_v$ distributions are a reasonable approximation to the natural

![Figure 4.17](image-url)

*Figure 4.17. Comparison between the (a) best-fit bend angle distribution (section 4.8) for the (1,1,1) and (1,2,1) Coulomb explosion channels and (b) the results of the MCSCF calculation of the geometry of the exploding $H_2O^{3+}$ and $H_2O^{4+}$ ions of Werner et al (1995) following ionization by HCl impact.*
bend angle distributions. Examining the results in figure 4.17(b), it would appear that the molecular ions generated during the laser-H$_2$O interaction undergo large bending motions. These motions are considerably larger than that expected in the neutral ground state molecule, as discussed earlier. However, there is a distinct difference between the results in figure 4.17(a) and (b), in that the bend angle distribution in the laser-H$_2$O reaction does not return to zero around 180°. In fact, there is an equal probability of finding the molecule at 130° or 180° for the (1,1,1) channel, and similarly between 140° and 180° for the (1,2,1) channel. It would therefore appear that the observed bend angle distributions (figure 4.17a) are not caused by the natural geometry of the exploding molecule.

In the present work the observation of high probabilities for large bend angles, between 130° and 180°, strongly indicates that the molecules have been straightened in the laser field. The phenomenon responsible for this straightening of the molecule may be bend angle softening, tentative evidence for which has been found in the

**Figure 4.18.** Excitation scheme for bend angle softening in the H$_2$O$^+$ ion in a 790 nm laser field.
photoelectron spectrum of H$_2$O at 532 nm (Rottke et al 1998).

In figure 4.18, the bending potential energy curve of H$_2$O$^+$, as published by Rottke et al 1998, is shown. The molecular ion is assumed to be in the ground state (X $^2$B$_1$). Through single photon absorption (in the present laser conditions, equivalent to an energy of 1.6 eV), the ground state of the molecular ion may couple to the excited A $^2$A$_1$ state, which is linear. Following one or more large-scale oscillations in the excited state, the molecule may return to the ground state through the emission of one photon. This process is analogous to two-photon dissociation of the H$_2^+$ molecular ion, as discussed in chapter 1.

To allow a direct comparison, figure 4.19 shows the result of lowering the excited state bending potential by the photon energy.

![Diagram showing the change in bond angle with energy](image)

**Figure 4.19.** Bend angle softening illustrated by dressing the excited state by the photon energy.

The time scale for this motion is comparable to the rise time of the laser pulse. If the molecule is ionized near the start of the laser pulse, which is likely (Posthumus et al 1996, Thompson et al 1997), then there is enough time for the ion to undergo this
bending process before the peak intensity is reached, and Coulomb explosion takes place. The bend angle distribution would be modified in this process, increasing the importance of large angles as observed.

4.12 Summary

In $\text{H}_2\text{O}$, ion momentum imaging coupled with Monte Carlo simulation was used to quantify the geometry of the exploding molecule. It was found that the experimental results were well-reproduced by a bond length distribution peaking at double the equilibrium separation, indicative of enhanced ionization. A narrowing of the angular width of the emitted ions with increasing channel indicated that laser induced reorientation occurs. Treating the molecule as a rigid rotor suggested that reorientation could occur within a few oscillations of the laser pulse. The best-fit bend angle distribution indicated that the $\text{H}_2\text{O}$ molecule was not behaving as expected from its ground state configuration, rather that the laser field was exciting a large-scale bending motions. It was concluded that one photon dressing of the bending potential of the $\text{H}_2\text{O}^+$ molecular ion occurs.
Chapter 5. Laser-induced Coulomb explosion, geometry modification and reorientation of CO$_2$

5.1 Introduction

This chapter will describe experimental investigations of laser-induced Coulomb explosion, reorientation and geometry modification in carbon dioxide using the experimental methods and data processing techniques discussed in chapters 2 and 3. Firstly, the covariance mapping technique (Frasinski et al 1989, chapter 3) is used to identify the Coulomb explosion channels, and then the reorientation of the CO$_2$ molecule is investigated in detail. Finally, ion-momentum imaging (IMI) coupled with Monte Carlo simulation is employed to quantify the geometry of the molecule during Coulomb explosion. The implications of the simulation results will be discussed within the current understanding of laser-induced field ionization of triatomic molecules.

Within this chapter, a variety of laser intensities are used, however, table 5.1 summarises those parameters that are constant throughout.

<table>
<thead>
<tr>
<th>Table 5.1. Beam parameters of laser-CO$_2$ studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser parameter</td>
</tr>
<tr>
<td>Wavelength</td>
</tr>
<tr>
<td>Pulse duration</td>
</tr>
<tr>
<td>Beam diameter</td>
</tr>
<tr>
<td>Focussing</td>
</tr>
<tr>
<td>Peak intensity</td>
</tr>
</tbody>
</table>

5.2 Preparation of CO$_2$ target

The carbon dioxide target gas is introduced into the TOFMS through the hypodermic needle as discussed in chapter 2. The UHV needle valve, which controls flow into the vacuum chamber, is closed and the entire stainless steel gas line is evacuated to a base pressure of $1 \times 10^{-3}$ Torr. The lecture bottle, containing 99.99 % pure carbon dioxide is opened, flooding the gas line. The value to the diaphragm pump is then closed, and the UHV needle valve opened, allowing the target gas into the chamber. Importantly, as described in chapter 2, different fill pressures are required depending on the type of experiment being performed. While performing covariance mapping, the TOFMS is filled to around $2 \times 10^{-9}$ Torr, to ensure no more than a few molecules in the laser focus per laser shot. In the case of the reorientation and momentum imaging experiments, the fill pressure is of the order of $10^{-7}$ Torr.
An example of a TOF spectrum recorded at a fill pressure of $1 \times 10^{-7}$ Torr, and a laser intensity of $3 \times 10^{16}$ Wcm$^{-2}$ is shown in figure 5.1. Unlike in the previous chapter, the Coulomb explosion of carbon dioxide is considerably more complex: as can be seen, the atomic constituents can be as much as triply ionized, corresponding to the explosion of CO$_2^{9+}$. As a consequence, the number of possible Coulomb explosion channels is far higher. Therefore, a particular ion peak in the TOF spectrum may originate from a number of channels. For example, as many as nine channels have been observed involving the O$_2^{2+}$ ion. Therefore, it is not possible to assign the explosion channels simply by estimating the kinetic energy release from around double the equilibrium separation. It is necessary to resolve the explosion channels. This is discussed in the following section.

![Time-of-flight spectrum of laser-CO$_2$ interaction](image)

**Figure 5.1.** Time-of-flight spectrum of laser-CO$_2$ interaction generated by 55 fs laser pulses focussed to generate an intensity of $3 \times 10^{16}$ Wcm$^{-2}$. The laser wavelength was 790 nm, and the extraction field was 300 V/cm.

5.3 **Covariance mapping**

As discussed in section 1.6.1, a number of 'channel resolved' experiments employing covariance mapping or coincidence detection have allowed identification of the explosion channels and measurement of the kinetic energy release (KER) in carbon dioxide. Cornaggia (1996) and Hering and Cornaggia (1999) employed
double-covariance, Cornaggia et al (1994) and Frasinski et al (1994) used triple-covariance, and Sanderson et al (1999b) used triple-coincidence in conjunction with a position- and time-sensitive detector. In these experiments, a range of molecule-field interaction times have been employed. Laser pulses of 40 fs (Hering and Cornaggia 1999), 150 fs (Cornaggia et al 1994 and Cornaggia 1996) and 200 fs (Frasinski et al 1994) and highly charged ion impact (with a molecule-field interaction time of the order of 1 fs) (Sanderson 1999b) were used. In this section, the Coulomb explosion channels observed are presented, and the total kinetic energy release associated with each channel determined by two-dimensional covariance mapping.

In this experiment, the laser polarisation was set parallel to the axis of the TOFMS and the aperture was removed to ensure near-unit collection efficiency. The number of laser pulses and hence number of individual TOF spectra recorded was of the order of $10^4$. In this experiment, an intensity of $3 \times 10^{16}$ Wcm$^{-2}$ was used. By applying conservation-of-momentum to the explosion, i.e. measuring the momenta of pairs of correlated ions, the explosion channels may be identified. Figure 5.2 shows a covariance map covering the full range of ions produced, in which the ions

**Figure 5.2.** Covariance map of carbon dioxide recorded at a wavelength of 790 nm with 55 fs laser pulses focussed to generate intensities of $3 \times 10^{16}$ Wcm$^{-2}$. The laser polarization direction is parallel to the TOFMS axis, and the extraction field is 300 V/cm.
detected are labelled on the y-axis, using white dashed arrows. The subscripts f, m and b correspond to the 'forward', 'middle' and 'backward' ions. The average TOF spectrum is also shown in figure 5.2, to the left and below the covariance map.

A number of observations may be made concerning the covariance islands shown in figure 5.2. Firstly, the strongest channels involve the O$^{2+}$ ion (toward the bottom left of the map). Channels involving O$^+$ and O$^{3+}$ are present on the map, but are weaker. The CO$_2^{2+}$ → CO$^+$ + O$^+$ two-body explosion channel is also observed, but is weaker than all of the three-body processes. Also, the CO$_2^+$ ion appears to be correlated with all of the other ions generated by the laser-CO$_2$ interaction. These are all so-called 'false' correlations, and are due to CO$_2^+$ being generated in the wings of the laser focus in almost every laser pulse.

A second covariance map is presented in figures 5.3 and 5.4. These maps contain the atomic ions generated in the laser-CO$_2$ interaction. Both figures employ the same covariance data, but presented on two different z scales to illustrate the difference in channel strengths. In figure 5.3, the map is presented on a colour scale that highlights the highest order correlations, whereas figure 5.4 highlights the lower-order correlations.

**Figure 5.3.** Covariance map of carbon dioxide recorded under the same laser conditions as figure 5.2, but with an extraction field of 800 V/cm. The z-scale is adjusted to show the strongest correlation islands.
The channel identification procedure is demonstrated in the figure 5.4, where the vertical solid white line links the following correlations: (a) $\text{O}^+ + \text{O}^+$, (b) $\text{O}^+ + \text{C}^+$, (c) $\text{O}^+ + \text{O}^{2+}$ and (d) $\text{O}^+ + \text{C}^{2+}$. The line corresponds to the peak of correlation (a), which passes through the peak of correlation (b); correlations (c) and (d) are observed to peak at higher momenta. Correlations (a) and (b) therefore constitute a Coulomb explosion channel, as momentum is conserved in the oxygen ions; this is the $\text{CO}_2^{3+} \rightarrow \text{O}^+ + \text{C}^+ + \text{O}^+$ channel. All of the explosion channels identified in this manner are presented in table 5.2 along with the total kinetic energy released (KER) and the Coulombic kinetic energy (CKE) from the ground state equilibrium position. The notation $(M, N, P)$ in table 5.2 corresponds to the explosion channel:

$$\text{CO}_2^{(M+N+P)+} \rightarrow \text{O}^{M+} + \text{C}^{N+} + \text{O}^{P+}$$

Equation 5.1

The Coulombic kinetic energy (in eV) is calculated using equation 5.2:

$$\text{CKE} = \frac{14.4MN}{r_1} + \frac{14.4NP}{r_2} + \frac{14.4MP}{r_1 + r_2}$$

Equation 5.2

where $M$, $N$ and $P$ are the ion charges in atomic units (according to equation 5.1),
Table 5.2. Measured KER for the Coulomb explosion channels identified by two-dimensional covariance mapping. The experimental values are then compared to the CKE generated by explosion of the ground state equilibrium position. The ratio of these two values in then compared with those measured in references [a] to [e] (see below). Kav is the mean k over all observed channels for each pulse duration.

<table>
<thead>
<tr>
<th>Channel (M,N,P)</th>
<th>KER (eV)</th>
<th>CKE (eV)</th>
<th>200fs [a]</th>
<th>150fs [b]</th>
<th>55fs (present)</th>
<th>40fs [c]</th>
<th>1fs [d, e]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,1,1)</td>
<td>18</td>
<td>31</td>
<td>0.55</td>
<td>0.58</td>
<td>0.55</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>(1,1,2)</td>
<td>50</td>
<td>0.54</td>
<td>0.51</td>
<td>1.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1,2,1)</td>
<td>56</td>
<td>0.61</td>
<td></td>
<td>1.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1,2,2)</td>
<td>38</td>
<td>87</td>
<td>0.38</td>
<td>0.44</td>
<td>1.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2,1,2)</td>
<td>42</td>
<td>74</td>
<td>0.57</td>
<td>0.57</td>
<td>0.51</td>
<td>1.20</td>
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<tr>
<td>(2,2,2)</td>
<td>70</td>
<td>124</td>
<td>0.51</td>
<td>0.56</td>
<td>0.55</td>
<td>1.22</td>
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<tr>
<td>(2,2,3)</td>
<td>90</td>
<td>161</td>
<td>0.57</td>
<td>0.56</td>
<td>0.55</td>
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<td></td>
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<tr>
<td>(2,3,2)</td>
<td>174</td>
<td>0.50</td>
<td></td>
<td>0.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2,3,3)</td>
<td>100</td>
<td>223</td>
<td>0.45</td>
<td>0.45</td>
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<td></td>
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</tr>
<tr>
<td>(3,3,3)</td>
<td>116</td>
<td>279</td>
<td>0.39</td>
<td>0.47</td>
<td>0.42</td>
<td>0.51</td>
<td></td>
</tr>
</tbody>
</table>

k\(=\)KER\(\div\)CKE

- k\(_{AV}\) = 0.5, 0.5, 0.51, 0.54, 1.33

[a] Frasinski et al 1994
[b] Cornaggia et al 1994
[c] Hering and Cornaggia 1999
[d] Sanderson 1999b
[e] Nishide 1999

and \(r_1\) and \(r_2\) are the internuclear separations between the carbon and the two oxygen ions, in angstroms. The results of Frasinski et al (1994), Cornaggia et al (1994), Cornaggia (1996), Hering and Cornaggia (1999) and Sanderson et al (1999b) are also included.

Comparing the ratio of \(k = \text{KER} / \text{CKE}\) from the present work with those from Frasinski et al (1994), Cornaggia et al (1994), Cornaggia (1996), Hering and Cornaggia (1999) and Sanderson et al (1999b), the same general trend is observed: \(k\) decreases slightly with increasing pulse length. In the highly-charged ion (HCI) experiment (Sanderson et al 1999b), roughly the same range of channels was observed (Nishide 1999) although the KER has only been calculated for those channels reported. The values of \(k\) observed in the present and previous laser experiments show some scatter, but an average taken across all channels shows a small systematic increase in \(k\) with decreasing pulse length. This observation is in agreement with the behaviour of diatomic molecules field ionised by 400fs and 50fs laser pulses (Posthumus et al 1996a). The relatively small magnitude of the increase is due to the importance of the critical distance, \(r_c\) (See Posthumus et al 1996ab, Seideman et al 1995 and Zuo and Bandrauk 1995, and discussion in sections 1.3 and 1.4).

The results from the HCI experiment (Sanderson et al 1999b) are interesting as they
show $k > 1$, where explosion has occurred from around the ground state equilibrium position. The HCI impact can be viewed as a unidirectional electric field pulse in which the HCI-molecule interaction time is around 1 fs, causing field ionisation. Although interactions between the HCI and molecule such as momentum transfer complicate the situation, this observation indicates that the dominance of the critical distance in field ionisation could be overcome with a laser pulse of a few femtoseconds in duration. In this case, Coulomb explosion will occur from the ground state equilibrium position.

The channel information and KER information gained from this experiment will be utilised in later sections, where the IMI technique is used to study the geometry of the exploding molecule.

5.4 Laser-induced reorientation

In section 1.5, a number of recent experimental and theoretical investigations into laser-induced molecular reorientation were discussed. Two of the most recent publications concerning this subject have demonstrated reorientation in a number of light diatomics ($\text{H}_2$ and $\text{N}_2$ in Posthumus et al 1998 and $\text{O}_2$ and $\text{Cl}_2$ in Ellert et al 1998), and have shown that the heavy $\text{I}_2$ molecule is not reorientated. However, laser-induced reorientation in triatomics has not been the subject of as many investigations. In Sanderson et al 1998b, the narrowing of a fitted distribution ($\text{Acos}^{n}\beta$) with explosion channel was taken to infer reorientation in carbon dioxide, where $\beta$ is the angle between the laser polarisation and the axis of the TOFMS, and A as an arbitrary scaling parameter. We reported that $n$ increased from $n = 12$ for the (1,1,1) channel to $n = 16$ for the (2,3,2) channel. However, the distinction has not been made experimentally between laser-induced reorientation and preferential-ionisation of initially aligned molecules.

In this section, the experimental technique described in Ellert et al 1998 is applied to carbon dioxide. Furthermore, the degree of reorientation is quantified. The experimental technique used to investigate reorientation is as follows.

Firstly, a time-of-flight spectrum was recorded with linear polarisation, at a pulse energy of 450 $\mu$J with the polarisation direction set parallel to the axis of the TOFMS. The aperture was present in the spectrometer, thus only ions from those molecules that exploded along the TOF axis within the angular acceptance $\varphi_{acc}$ are
observed. The pulse energy was then doubled to 900 μJ, and a quarter-wave plate inserted into the beam path to produce circular polarisation. A second time-of-flight spectrum was then recorded with circular polarisation.

The circularity of the polarisation was tested by placing a linear polarizer after the quarter-wave plate, and measuring the laser pulse energy as a function of polarizer angle. The pulse energy was found to be constant to within 5%, indicating good circularity.

Presented in figure 5.5 are the TOF spectra of carbon dioxide recorded with linear and circular polarisation. Comparing the peak heights throughout both spectra, the following observations may be made. The average ion signal strength of the CO$_2^+$ parent ion is comparable in both cases. However, for all other stages of ionisation, the spectrum recorded with linear polarisation exhibits a significant increase in ion signal. The straightforward conclusion from figure 5.5 is that carbon dioxide is substantially reorientated during the interaction with the laser pulse.

To quantify the relative degree of reorientation for each ion species, the ratio of the integral ion signal for linear to circular polarisation is calculated. This ratio shall be referred to as the reorientation ratio, $R_{\text{rot}}$. The variation of $R_{\text{rot}}$ with ion species is

![Figure 5.5](image-url)

**Figure 5.5.** Time-of-flight spectra of laser-CO$_2$ interaction with (solid line) linearly polarized 450 μJ pulses and (dashed line) circularly polarized 900 μJ pulses. In both cases, the pulse duration is 55 fs and the extraction field was 300 V/cm. The increase in ion signal with linear polarized pulses indicated reorientation is occurring.
presented in figure 5.6.

Before discussing the implications of figure 5.6, a distinction is made between the four different types of ions generated by the laser-CO\textsubscript{2} interaction. In increasing energy, the following types of ions are observed:

- \text{CO}_{2}^{+} and \text{CO}_{2}^{2+}: thermal carbon dioxide ions, generated by the single- and double-ionization of the target molecule. These ions are indicated by the dotted line on figure 5.6.

- \text{CO}^{+}_{m} and \text{O}^{+}_{m}: low momentum ions from the dissociative ionization of carbon dioxide. These ions originate from the following channels: \text{CO}_{2}^{+} \rightarrow \text{CO}^{+} + \text{O} and \text{CO}_{2}^{+} \rightarrow \text{CO} + \text{O}^{+}. These ions are indicated by the short dashed line on figure 5.6.

- \text{C}^{p+} (p = 1, 2, 3): low momentum carbon ions from three-body Coulomb explosion of \text{CO}_{2}. These ions are indicated by the long dashed line on figure 5.6.

- \text{O}^{q+} (q = 1, 2, 3) and \text{CO}^{+}_{b}: high momentum oxygen and carbon monoxide ions from the Coulomb explosion of \text{CO}_{2}. These ions are indicated by the solid line on figure 5.6.

![Figure 5.6](image-url)

**Figure 5.6.** Ratio of relative ion signal for measured with linear and circular polarization as shown in figure 5.5.
It should be pointed out that the two-body channel is a dissociative channel, however, it was found that this channel behaved in a manner more akin to the three-body Coulombic channels, rather than the dissociative channels mentioned above. The ionization process depends on the type of laser polarization used. To understand the implications of figures 5.5 and 5.6, it is necessary to discuss the similarities and differences between the two processes.

Common to both polarization types is the manner in which ionization is maximised. In both cases, the highest stage reached depends on the maximum magnitude of the laser $\varepsilon$-field along the O-O axis (Codling et al 1987, as shown in figure 1.4). Bearing this in mind, the dependence of the ionization on the location and initial orientation of the molecule is discussed for both polarization types.

- **Circular polarization**: The ionization is governed purely by the location of the molecule within the laser focus, as the electric field is equal in all directions. In this case, the molecules effectively sample the laser intensity.

- **Linear polarization**: The ionization is governed not only by the location of the molecule within the focus, but also by the initial alignment of the molecule with respect to the polarization direction.

Considering two possibilities for the linear case:

- **$\text{CO}_2$ is not reorientated**: molecules that are well aligned with the electric field will be most heavily ionized. This is referred to as 'preferential ionization'. Misaligned molecules will experience a weaker field, hence will be ionized into lower channels. This process would lead to the characteristic distribution of ions around the polarization direction.

- **$\text{CO}_2$ is reorientated**: the reorientation process increases the number of molecules that are well aligned with the field. This will increase the ion signal throughout the TOF spectrum.

We should also consider the effect of the detector acceptance angle, $\varphi_{\text{acc}}$ on the TOF spectrum. Two processes are possible in the present experiment. In the case of the low momentum ions, the detector acceptance angle $\varphi_{\text{acc}} = 90^\circ$, hence all ions are collected. As the electric field is isotropic in the case of the circular polarization, more of these low momentum ions are generated. Hence, if carbon dioxide is not reorientated by the linearly polarized pulses, there will be more signal for the low momentum ions in the circular case.
The situation for the high momentum ions is simpler because the number of molecules coincidentally within the angular acceptance of the detector is identical in both cases, and the e-field parallel to the TOF axis has been made the same. Hence, if there is no reorientation, the high momentum ions that reach the detector will have been generated in identical conditions. Hence, if carbon dioxide is not reoriented, the ion signal from the high momentum ions will be identical to that from the linear polarization. Conversely, if reorientation does occur, there will be an increase in the ion signal with the linear polarization. This is the signature of reorientation.

At this point, the effect of the variation of $\phi_{acc}$ with ion momentum is quantified. This variation has been calculated for the CO$_2^+$ and O$q^+$ ($q = 1, 2, 3$) ions, and is illustrated in figure 5.7. In the case of CO$_2^+$, the ion momentum $p < 2 \times 10^4$ amu ms$^{-1}$, hence $\phi_{acc} = 90^\circ$ for all ions. However, because of the Coulomb explosion process, the momentum of the oxygen ions is considerably higher. Using the covariance maps presented in section 5.3, typical momenta for the oxygen ions have been calculated. These values are: $p(O^+) \approx 150 \times 10^3$ amu ms$^{-1}$, $p(O^{2+}) \approx 300 \times 10^3$ amu ms$^{-1}$ and $p(O^{3+}) \approx 450 \times 10^3$ amu ms$^{-1}$. The corresponding $\phi_{acc}$ of ions of these momenta are presented on the insert of figure 5.7. As can be seen, there is actually a

![Figure 5.7](image_url)

**Figure 5.7.** Variation of detector acceptance angle with ion species and momentum for CO$_2^+$ and O$q^+$ ($q = 1, 2, 3$). The insert shows the measured peak momenta for the oxygen ions.
decrease in $\varphi_{\text{acc}}$ from $O^+$ to $O^{3+}$, despite the fact that $\varphi_{\text{acc}}$ increases with oxygen ion charge for a particular momentum.

The implication of this observation is that if the reorientation process is strong, but independent of channel, $R_{\text{rot}}$ will be smaller for a low momentum ion as compared to a high momentum ion. This is because $\varphi_{\text{acc}}$ is larger, hence more of the isotropic ions from the circularly polarized laser pulses will be detected.

Bearing in mind these observations, we return to figure 5.6 and examine the variation of $R_{\text{rot}}$ with ion species.

- For the lowest stage of ionisation present ($\text{CO}_2^+$), $R_{\text{rot}} \approx 1$. Therefore, even for this low-intensity process, reorientation occurs. Without reorientation, there would be substantially more $\text{CO}_2^+$ signal with the circular polarisation as discussed above.

- The production of $\text{CO}_2^{2+}$ is enhanced by the linear polarisation, which indicates that reorientation is more influential for this ion as compared to $\text{CO}_2^+$.

- The dissociative ionisation of $\text{CO}_2^+$ into $\text{CO}^+_m + \text{O}$ or $\text{CO} + \text{O}^+_m$ shows a further enhancement in ion signal with the linear polarisation, where $2.5 < R_{\text{rot}} < 3$.

- In the case of the carbon ions, there is a decrease in $R_{\text{rot}}$, from $R_{\text{rot}} = 3.1$ for the $\text{C}^+$ ion, to $R_{\text{rot}} = 1.7$ for the $\text{C}^{3+}$ ion. This observation indicates that, in the case of the low-energy ions, the maximum amount of reorientation occurs when the molecule explodes into channels producing the $\text{C}^+$ ion.

- In the case of the energetic ions, a similar maximum is observed for the singularly charged oxygen ions. For the $\text{CO}^+_b$ ion from the (1,1) channel, $R_{\text{rot}} = 3.8$, then rising to a maximum at $R_{\text{rot}} = 6.3$ for the $\text{O}^+_f$ ion, then decreasing to $R_{\text{rot}} = 4.4$ for the $\text{O}^{3+}_f$ ion. This effect is not due to the change in $\varphi_{\text{acc}}$ with charge state, as previously discussed.

The dependence of $R_{\text{rot}}$ on ion species indicates that most reorientation is experienced by molecules that explode into the (1,1,1) channel (i.e. the $\text{O}^+$ and $\text{C}^+$ ions); the importance of this process decreases for the higher-order channels which involve the $\text{O}^{2+}$, $\text{O}^{3+}$, $\text{C}^{2+}$ and $\text{C}^{3+}$ ions.

As pointed out chiefly by Posthumus et al 1996 and Seideman et al 1995 (molecular ionization) and Lambropoulos 1985 (atomic ionization), the ionization process is ongoing throughout the rising edge of the laser pulse. Hence it appears from the current results that laser-induced reorientation in $\text{CO}_2$ is strongly coupled to the
ionization process up to the point at which the third electron is removed. For higher stages of ionization, it appears that reorientation 'looses out' to the ionization process, which will increasingly occur through preferential ionization of the well-aligned molecules. In other words, molecules that experience a weak electric field (either through being badly aligned with the polarization or through being in a low-intensity region of the focus) are reorientated heavily by the field, and the ionization process is maximised by this reorientation. However, molecules experiencing a strong electric field are strongly reorientated until the removal of the third electron, then further ionized to the higher channels, depending on their alignment with the field at this point within the pulse.

The implication of the results from this section will be discussed later, following the simulation of the Coulomb explosion of the molecule. Specifically, laser-induced reorientation will be covered in section 5.13.

5.5 TOF matrix of CO$_2$

Following the investigation of the ionization mechanics and laser-induced reorientation of carbon dioxide, the geometry of the exploding molecule is now investigated. As in the case of water (chapter 4), the geometry of the exploding molecule is quantified in a four-step process. Firstly a TOF matrix is recorded, then parts of this matrix are converted into IMI maps, then the 'finite angle' correction applied, and finally the explosion process is simulated using the Monte Carlo technique.

A TOF matrix is recorded using 55 fs 790 nm laser pulses focussed to generate an intensity of $3 \times 10^{16}$ Wcm$^{-2}$. This is presented in figure 5.8(a), as a function of time-of-flight (x-axis) and the angle between the laser polarization direction and the TOFMS axis, $\beta$ (y-axis). To aid ion identification, a horizontal section through the TOF matrix at $\beta = 0^\circ$ is shown below in figure 5.8(b). A number of qualitative observations may be made from figure 5.8 concerning the low-energy ions. The CO$_2^+$ parent ion, CO$_2^{2+}$ doubly ionized parent ion and the low energy CO$^+$ and O$^+_m$ ions are independent of $\beta$. These ions are either thermal (CO$_2^+$ and CO$_2^{2+}$) or from dissociative ionization (CO$^+_m$ and O$^+_m$) hence have low momentum. As discussed earlier, the ion signal from these ions peaks at the zero-momentum flight time.

An expanded section of the TOF matrix is shown in figure 5.9, showing the atomic
ions arising from the laser-CO₂ interaction. All of the atomic ions exhibit anisotropy to varying extents. The most striking feature is the distribution of the oxygen ion, which are strongly peaked around β = 0° and 180°, hence the oxygen ion signal is maximised when the polarization direction is parallel to the TOFMS axis. As observed in sections 5.2 and 5.3, the oxygen ions have considerable momentum, hence have strong forwards-backwards structure.

The carbon ions in figure 5.9(a) are peaked around the zero momentum flight time. These ions exhibit a more subtle anisotropy than the oxygen ions. The C⁺ ion is seen to broaden slightly when β = ±90° and 270°, which is when the polarization direction is perpendicular to the TOFMS axis.

There is a more pronounced broadening for the C³⁺ ions around the same β angles. However, the signal from the C²⁺ ions is more complex. In addition to broadening around β = ±90° and 270°, there is a distinct broadening around β = 0° and 180°. Therefore, the C²⁺ ion appears to behave as a hybrid of the oxygen and carbon ions. This may be explained by re-examining figure 5.4, where the O²⁺ + O³⁺ correlation
islands are highlighted by a white rectangle. The covariance maps shows that, for an extraction of 800V the C$^{2+}$ and O$^{3+}$ ions are very close, and at 300V overlap. Following earlier observations, it is fair to say that the broadening around $\beta = 0^\circ$ and $180^\circ$ is due to the O$^{3+}$ ion, and around $\beta = \pm 90^\circ$ and $270^\circ$ is due to the C$^{2+}$ ion.

The ion signal as a TOF matrix is a useful visualisation tool. However, to gain a better understanding of the explosion process, it is necessary to display the TOF data as an ion-momentum image.

### 5.6 Uncorrected CO$_2$ IMI maps

As in the previous chapter, ion-momentum images are created by displaying sections of the TOF matrix from the flight time corresponding to a momentum range of $p = 0$ to $600 \times 10^3$ amu ms$^{-1}$. The radius of the plot is proportional to ion momentum and the polar axis is then simply the angle $\beta$. IMI plots are presented for all atomic ions in figures 5.10 and 5.11: the oxygen ions are presented in figures 5.10(a)-(c), the carbon ions in figures 5.11(a)-(c). The arrow indicates the laser polarisation direction.
Figure 5.10. Uncorrected $O^q$ ($q = 1,2,3$) IMI maps for the atomic fragment ions resulting from the Coulomb explosion of CO$_2$. The arrow shows the laser polarization direction.
Figure 5.11. Uncorrected C\(^p\) (p = 1,2,3) IMI maps for the atomic fragment ions resulting from the Coulomb explosion of CO\(_2\). The arrow shows the laser polarization direction.
(e) which corresponds to $\beta = 0^\circ$ and $180^\circ$. In all cases, the radial distance is ion momentum $p \ (10^3 \text{ amu ms}^{-1})$, therefore the centre of the IMI plots is at $p = 0$, and the circular edge of each plot is $p = 600 \times 10^3 \text{ amu ms}^{-1}$. The z-axis is the ion signal in arbitrary units, presented on a colour scale. In figure 5.10(a), the high-momentum ring around the edge of the plot is an overlap with the C$^+$ ion. A similar overlap applies to figure 5.11(a), where the C$^+$ signal is the central distribution around $p = 0$, and the two high intensity signals at the top and bottom are due to an overlap with the O$^{2+}$ ions.

By considering the range of momenta in the IMI plots over all oxygen ions, we can derive information about the Coulomb channels that occur. This is possible because the oxygen ions take away the majority of the momentum, as the carbon atom is in the middle of the molecule. As an example, the highest momentum with which O$^+$ ions are detected (see figure 5.10(a)) is $300 \times 10^3 \text{ amu ms}^{-1}$; this is near to the middle of the momentum range of the O$^{2+}$ signal in Fig 5.10(b). We can therefore deduce that explosion channels involving O$^+$ and O$^{2+}$ such as (1,1,2) or (1,2,2) are occurring. However, there is no overlap in momentum between the O$^+$ and O$^{3+}$ ions, so we deduce that no channels involving these ions are occurring. Both of these conclusions agree with the information gained from covariance mapping in section 5.3.

By comparing fragment ion momenta we can gain an insight into the origin of the two rings present on the O$^+$ IMI plot at $p = 100 \times 10^3 \text{ amu ms}^{-1}$ and $p = 280 \times 10^3 \text{ amu ms}^{-1}$ in Fig 5.10(a). These rings are not present in either the O$^{2+}$ or O$^{3+}$ plots, nor are they present in the CO$^+$ IMI, which is not shown. Furthermore, they can not originate from a symmetric O$^+ + O^+$ channel (for example, the (1,1,1) channel) as the O$^+$ ion momentum will lie in the momentum range between the two rings, as derived from the covariance mapping experiment. This implies that these signals are not due to O$^+$ from any explosion or dissociation channel. Further analysis has shown that the positions of these features correspond to $p = 0$ for the multiply charged ions CO$^{2+}$ (inner ring) and CO$_2^{3+}$ (outer ring) on the TOF matrix. The presence of the residual CO$_2^{3+}$ signal is not surprising, as recent experiments have shown that femtosecond laser pulses may produce metastable triply charged parent ions (Sakai et al 1998). The presence of CO$^{2+}$ is more puzzling, as it has no recoil momentum, the ion signal is at a maximum at $p = 0$. This ion must therefore be produced either in an
asymmetric process $\text{CO}_2^{2+} \rightarrow \text{CO}^{2+} + \text{O}$ or as the result of the sequential process $\text{CO}_2^+ \rightarrow \text{CO}^+ + \text{O}$ followed by $\text{CO}^+ \rightarrow \text{CO}^{2+}$. The sequential process is more plausible, as no evidence has been found of any other channels in which the exploding ions differ in charge by more than one unit, as seen in table 5.2. The presence of $\text{CO}^{2+}$ probably explains the signal observed by Sanderson et al (1998), as shown in appendix 7.3. In that work, the low-energy $\text{O}^+$ signal exhibited a second maximum perpendicular to the laser polarisation direction ($\beta = \pm 90^\circ$ and $\beta = 270^\circ$) and was tentatively assigned to molecules reorientated in this direction and drastically bent. However, the superior resolution in both angle and momentum in the present experiment now allows us to rule out this conclusion.

The IMI plots presented in figures 5.10 and 5.11 can be interpreted in terms of the geometry of the exploding carbon dioxide molecule. If the molecule is linear and the two O-C bonds break simultaneously, the carbon ions will receive no initial momentum from Coulomb explosion except from asymmetric channels, which will result in carbon ions being emitted along the O-C-O axis. However, if the molecule has a bent geometry, the carbon ion will receive significant momentum perpendicular to the O-O axis. In the case of $\text{C}^+$, $\text{C}^{2+}$ and $\text{C}^{3+}$ ions, the peak in the ion signal is at zero momentum, and the momentum islands are elliptical, the major axes of which are perpendicular to the momentum of the oxygen ions. An uncritical interpretation of figures 5.10 and 5.11 leads to the conclusion that there is a distribution of bend-angles peaked at $\theta = 180^\circ$.

### 5.7 Corrected $\text{CO}_2$ IMI maps

As was shown in the previous chapter, applying the finite angle correction to the IMI maps dramatically altered the distribution of the central (oxygen) ions, whereas the effect on the terminal (hydrogen) ions was a great deal less. With this observation in mind, the finite angle correction is now applied to the IMI maps in figures 5.10 and 5.11. From the observations on $\text{H}_2\text{O}$, it is expected that the carbon ions will be affected the most.

Figures 5.12 and 5.13 show the result of applying the correction procedure to the IMI plots from figures 5.10 and 5.11. Again, the radial axis is $p$ (10$^3$ amu ms$^{-1}$), and the $z$-axis is the corrected ion signal in arbitrary units on a colour scale.

As discussed earlier, there is an overlap between the $\text{C}^{2+}$ and $\text{O}^{3+}$ ions. In figure
Figure 5.12. Corrected $O^q$ ($q = 1,2,3$) IMI maps for the atomic fragment ions resulting from the Coulomb explosion of $CO_2$. The arrow shows the laser polarization direction.
Figure 5.13. Corrected $C^p$ ($p = 1, 2, 3$) IMI maps for the atomic fragment ions resulting from the Coulomb explosion of $CO_2$. The arrow shows the laser polarization direction.
5.13(b), this contribution has been removed by scaling the \(O^{3+}_f\) signal by the ratio between the \(O^{2+}_f\) and \(O^{2+}_b\) ions, then reflecting around \(p = 0\) for the \(O^{3+}\) ions, and subtracting from the \(C^{2+}\) signal. The effect of this subtraction is seen by comparing figure 5.13(b) with 5.14, where figure 5.14 is the corrected but unsubtracted \(C^{2+}\) signal.

The high intensity (red) areas around the circumference of figures 5.12(a) and 5.13(a) and (b) are unrelated to the ion in question as with figures 5.10 and 5.11; these signals are due to other ion species. The fully resolved distributions of the fragment ions are now observed for the first time. As expected, the carbon ions are most affected by the finite angle correction. The peaks in the ion signal are now found at \(p = 50, 120\) and \(180 \times 10^3\) amu ms\(^{-1}\) for \(C^+\), \(C^{2+}\) and \(C^{3+}\) respectively, as opposed to at \(p = 0\) as in figure 5.11.

The correction procedure is less dramatic in the case of the oxygen ions except the low momentum \(O^+\) ion. However, this is to be expected, as the low momentum \(O^+\) signal from the \(CO + O^+\) dissociative channel, which is weak as compared to the three body Coulombic channels.

There is some ion signal parallel to the polarisation direction on the \(C^+\) IMI (figure 5.13(a)). Although it is tempting to interpret this as the consequence of molecules being aligned \textit{perpendicular} to the laser polarisation, and link it with the inner ring on the \(O^+\) IMI (figure 5.12(a)), the \(O^+\) signal does not vary as a function of angle in the same way as the \(C^+\) signal. As discussed earlier the inner ring on the \(O^+\) IMI plot...
is most likely to be due to CO$^{2+}$.

Two channels could be responsible for the C$^+$ signal parallel to the polarization direction. These are:

- Dissociation of CO$_2^+$ → CO$^+$ + O followed by enhanced ionization of CO$^+$ → C$^+$ + O$^+$.
- Enhanced ionization of CO$_2^+$ → CO$^+$ + O$^+$ followed by enhanced ionization of CO$^+$ → C$^+$ + O$^+$.

Both channels are possible, however, the interaction of the departing carbon ion with the oxygen atom or ion from the first step is examined to try to make a distinction. In the case of the first channel, the neutral oxygen atom will have low momentum (of the order of $20 \times 10^3$ amu ms$^{-1}$), but given the neutrality of the atom, the departing carbon ion will not interact with it. It is estimated that the Coulomb explosion of C$^+$ + O$^+$ (essentially Coulomb explosion of carbon monoxide) generates carbon and oxygen ions with a momentum of the order of $90 \times 10^3$ amu ms$^{-1}$. Given that the reorientation process will be strong for this channel, we would expect the carbon ions from this reaction to be strongly peaked around the polarization direction.

In the case of the second channel, the first stage has been observed to generate oxygen ions with a kinetic energy of 3.9 eV, and carbon monoxide ions with a kinetic energy of 2.2 eV (Frasinski et al 1994). Using a simplified version of the Monte Carlo software used in chapter 4, this channel was found to originate from a O$^+$ - CO$^+$ ion separation of 2.4 Å. It was found that, after 55 fs, the O-CO separation was 55 Å, with both ions travelling with a momentum of $110 \times 10^3$ amu ms$^{-1}$. If the CO$^+$ ion then Coulomb explodes, the reaction does not generate enough energy to allow the carbon ion to catch the lone oxygen ion. As a consequence the carbon ions will again be released along the polarization direction, but with considerably lower momentum than in the first channel, as the momentum of the carbon monoxide ion (from CO$_2^+$ → CO$^+$ + O$^+$) will combine with the momentum from the CO$^+$ → C$^+$ + O$^+$. These momenta are in opposite directions, hence will cancel, generating a carbon ion of negligible momentum.

This sequential process is dominant for long pulse experiments (Bhardwaj et al 1999), but only a residual signal can be seen at 55fs, and then only for the (1,0) channel of CO.

Multiple ionisation during the dissociation of CO$^+$ is not possible, as it originates
from a low intensity region. Clearly, in regions of high peak intensity, CO$_2^+$ may be formed in an electronic level which would dissociate into CO$^+$ + O, but as the laser field rises quickly there is insufficient time for the O-CO$^+$ bond to expand before further ionisation and dissociation takes place. This leads to the high-order Coulomb channels that result in three atomic ions with clearly correlated momentum.

A qualitative interpretation of the IMI plots in figures 5.12 and 5.13 can be drawn from the fact that the carbon ion distributions are not peaked at $p = 0$. The molecule must have a bend-angle distribution peaked at some angle $\theta \neq 180^\circ$ at the time of the Coulomb explosion. Furthermore, the linear configuration is very unlikely, as there is little ion signal at zero momentum in the case of the three carbon ions.

5.8 Monte Carlo simulation of Coulomb explosion of CO$_2$

To quantify the geometry of the exploding molecule, the Monte Carlo method demonstrated in chapter 4 is applied to carbon dioxide. As discussed earlier, the number of Coulomb channels occurring in the laser-CO$_2$ interaction is considerably higher than in the laser-H$_2$O case. Therefore, the simulation process is more time consuming. The essence of the simulation process is the same as described in chapter 4 and so only the salient points will be mentioned.

Before describing the simulation process, an important difference between the present work and all other laser-CO$_2$ experiments should be pointed out. In the work of Frasinski et al. 1994, Comaggia et al. 1994, Comaggia 1996 and Hering and Cornaggia 1999, the molecule was assumed to bend around an average linear geometry. In the present work, the publications of Herzberg 1966 and Sturge 1967 are used to generate the zero-point distribution as shown in figure 5.15. As can be seen from figure 5.15, the zero-point distribution is not peaked at a bend angle of 180$^\circ$, rather at $\theta = 174^\circ$. Although this distribution indicates that the molecule is very nearly linear, the important implication is that the number of molecules that are completely linear is negligible. This conclusion has especially important implications to the results of Cornaggia 1996 and Hishikawa et al. 1999: this will be discussed in section 5.12.

Also included in figure 5.15 is a linear approximation of the zero-point distribution, shown by the dashed line. This approximation will be used in the initial Monte Carlo simulations.
As in the case of H$_2$O, the initial conditions for the simulation were established, using a series of assumptions and earlier observations.

1. It has been shown that the Coulomb explosion of carbon dioxide occurs from around double the equilibrium separation, where the equilibrium separation $r_e = 1.16$ Å, hence it is reasonable to assume a Coulomb explosion from $r_c = 2.3$ Å.

2. The alignment distribution must peak around $\phi = 0^\circ$. The width of the alignment distribution was estimated by measuring the FWHM of the O$^q+$ ($q = 1, 2, 3$) ions at the peak momentum, and converting this to a FWAB for the $\phi$ distribution. For each of the ions, the following peak momenta and $\phi_{\text{wid}}$ were found: $p(O^+) = 200 \times 10^3$ amu ms$^{-1}$, $\phi_{\text{wid}} = 22^\circ$, $p(O^{2+}) = 300 \times 10^3$ amu ms$^{-1}$, $\phi_{\text{wid}} = 21^\circ$ and $p(O^{3+}) = 450 \times 10^3$ amu ms$^{-1}$.

3. It was assumed that the molecule explodes from around the peak in the ground state zero point distribution ($\theta_{\text{pk}} = 174^\circ$ Herzberg 1966, Sturge 1967). The width of the $\theta$ distribution is defined by $\theta_{\text{min}} = 165^\circ$, $\theta_{\text{max}} = 180^\circ$. This distribution is illustrated in figure 5.15.

These conditions are combined to generate a set of simulation parameters, which are summarised in figure 5.16. As can be seen, a bond length distribution of width $\pm 1$ Å was chosen, around $r_{\text{pk}} = 2.3$ Å. The (1,1,1), (2,2,2) and (3,3,3) channels were all
simulated using these parameters, and the results of these simulations are presented in figure 5.17, where 5000 iterations have been performed for each channel. Comparing the simulation results in figure 5.17 with the experimental results in figures 5.12 and 5.13, a number of observations may be made.

- The momentum of the simulated O$q^+$ (q = 1, 2, 3) ions is within the boundaries of the experimental data. However, considering that a number of channels contribute to each IMI maps, the O$^+$ ion momentum width appears to be too low (hence $r_{\text{wid}}$ was too low) and the O$^{3+}$ width is too high. It would therefore appear that there is a variation of $r_{\text{wid}}$ with ionization channel.

- The angular width of the O$^+$ ion is too low, indicating an underestimation of $\phi_{\text{wid}}$ for this ion. The agreement improves for the O$^{2+}$ ion, and for the O$^{3+}$ ion the agreement is very good, indicating that $\phi_{\text{wid}} = 20^\circ$ may be the lower limit of the alignment distribution.

- The momentum of the O$p^+$ (p = 1, 2, 3) ions is too low, indicating that $\theta_{pk} = 174^\circ$ is too near to $180^\circ$, and that $\theta_{\text{min}} = 165^\circ$ should be decreased. As the momentum range of the oxygen ions is of the right order, this momentum discrepancy is not
due to the bond length distribution.

- The angular width of the carbon ions is too low in all cases. This could be improved by increasing $\phi_{\text{width}}$, but the angular width of the $O^{2+}$ and $C^{3+}$ ions have shown that the alignment distribution cannot be used to compensate. However, it should be pointed out that considerable carbon ion momentum will be generated parallel to the O-O axis in the unsymmetrical channels such as (2,2,3).

To develop the simulation, the bend angle distribution was shifted to $\theta_{\text{pk}} = 170^\circ$, and $\theta_{\text{min}} = 160^\circ$, $\theta_{\text{max}} = 180^\circ$. This improved the fit of the carbon ions, but the quality of the oxygen ion fit was compromised. To counter this effect, the r-distribution was shifted from $r_{\text{pk}} = 2.3 \, \text{Å}$, $r_{\text{min}} = 1.2 \, \text{Å}$, $r_{\text{max}} = 3.2$ to $r_{\text{pk}} = 2 \, \text{Å}$, $r_{\text{min}} = 1 \, \text{Å}$, $r_{\text{max}} = 3$. This
recovered the momentum defect in the oxygen ions, and further improved the carbon ions.

Further small variations were made to the three distributions across 10 Coulomb channels. With each variation to the simulation parameters, the IMI maps for each ion were constructed from its constituent ions, and a visual comparison, followed by a least-squares fit, were made with the experimental data.

5.9 Simulation results
Following a large number of iterations of the simulation process, it was felt that the agreement between the experimental data and the simulated results could not be improved further. The final best-fit r, θ and φ distributions are presented in figures 5.18 to 5.20 respectively. A comparison between the corrected experimental data and the best-fit IMI maps are presented in figures 5.21 and 5.22 for the oxygen and carbon ions respectively. The agreement between the two types of result is good, indicating the validity of the technique.

![Figure 5.18. Best fit bond length distributions](image)

Figures 5.21 and 5.22 show the success of the simulation process, as the major features are well reproduced. Two simulated rings representing CO$_2^{3+}$ and CO$^{2+}$ were also included on figure 5.21(a) to aid visual comparison. The largest difference is in the angular width of the carbon ions. This difference could be
evidence for partially sequential dissociation. However, it was felt that to further improve the simulation process by taking into account the dissociation of the molecule early in the laser pulse would over-complicate the simulation, with minor gain.

As illustrated in figure 5.19, two trends are observed in the variation of the $r$-
Figure 5.21. Comparison between the corrected oxygen IMI maps (right-hand side) with the best fit IMI maps (left hand side)
Figure 5.22. Comparison between the corrected carbon IMI maps (bottom half of each pane) with the best fit IMI maps (top half of each pane).
distribution with Coulomb channel. Firstly, there is a narrowing of the distribution with increasing channel, and secondly, the peak in the distribution shifts to higher \( r \) for the highest three channels. More specifically, \( r_{\text{min}} \) is observed to increase slightly from 0.8 Å to 1 Å between the (2,2,3) and (2,3,2) channels. It is at this point that \( r_{\text{pk}} \) increases from \( r_{\text{pk}} = 2 \text{ Å} \) to \( r_{\text{pk}} = 2.2 \text{ Å} \). The variation of \( r_{\text{max}} \) is more disorderly than the other two parameters, however, a general trend of \( r_{\text{max}} \) decreasing from \( r_{\text{max}} = 5 \text{ Å} \) for the (1,1,1) channel to \( r_{\text{max}} = 3.7 \text{ Å} \) for the (3,3,3) channel.

Moving from the \( r \) distribution to the best-fit \( \theta \) distribution as shown in figure 5.20, a rather unexpected result is reported. Following extensive investigations into a large range of bend angle distributions, it was found that a single distribution could be used to generate all of the Coulomb channels. Examining the best-fit bend angle distribution in detail, it can be seen that it is similar in shape to the triangular approximation of the zero-point distribution shown in figure 5.15, but 'stretched' over a wider range of angles. The bend angle distribution was found to start at \( \theta_{\text{min}} = 150^\circ \), rising to a peak at \( \theta_{\text{pk}} = 171^\circ \), and falling to zero at \( \theta_{\text{max}} = 179^\circ \).

The variation of the alignment distribution with ionization channel, as shown in figure 5.20, involves a narrowing of the distribution of ions emitted for the laser-CO\(_2\) interaction with increasing charge state. It was found that \( \phi_{\text{wid}} \) decreased from \( \phi_{\text{wid}} = 30^\circ \) for the (1,1,1) to (2,1,2) channels, falling to \( \phi_{\text{wid}} = 25^\circ \) for the (1,2,2) to (2,2,3) channels, and further narrowing to \( \phi_{\text{wid}} = 20^\circ \) for the (2,3,2) to (3,3,3) channels.

5.10 Discussion of simulation results

Following the presentation of the simulation process it is necessary to compare these results with those of other experimental groups, and to understand them in the context of modern theoretical results. This will be discussed in the following sections, where each mechanism is discussed individually.

5.11 Discussion of simulation results - partially sequential dissociation

A number of observations from the corrected IMI maps and the simulation results give hints as to the manner in which the two O-C bonds extend. The simplest situation is when both bonds expand simultaneously. While being the easiest to deal with computationally, we believe that, for the lowest channels at least, the Coulomb explosion of the molecule is governed by the stability of the carbon monoxide ion.
formed by the dissociation of carbon dioxide.

Summarising results from the previous section, the following observations were made:

- The $\text{CO}_2^+ \rightarrow \text{CO}^+ + \text{O}^+$ channel has been observed in the covariance mapping experiment, as shown in figure 5.2. This is a very low intensity, low momentum process. The observation of $\text{CO}^+$ illustrates that the lowest energy process involves breaking only one bond.
- There is some evidence for $\text{C}^+$ ions parallel to the laser polarization direction (see figure 5.15(a)). As described in the discussion in section 5.7, it is most likely that these ions will originate from the $\text{CO}_2^+ \rightarrow \text{CO}^+ + \text{O}$ channel followed by $\text{CO}^+ \rightarrow \text{C}^+ + \text{O}^+$. However, this process will not be resolved in the covariance map, as the $\text{C}^+ + \text{O}^+$ correlation will be very weak, and will be strongly overlapped by the carbon and oxygen ions from the $(1,1,1)$ channel. To resolve this channel, it would be necessary to perform a comparison between an averaged TOF spectrum and the result of a two-body correlation experiment.
- The angular width of the simulated $\text{C}^+$ ions is lower than the corrected experimental results. However, the difference between the simulation and the experimental results decreases for the $\text{C}^{2+}$ and $\text{C}^{3+}$ ions. As mentioned before, the simulation is limited to simultaneous bond extension, so it therefore seems reasonable to say that partially sequential dissociation is of some importance for the lowest Coulomb channels, but negligible for the higher channels.
- There is considerable narrowing of the bond length distribution with increasing Coulomb channel, as shown in figure 5.21. This reinforces the observation of the previous point in that the evolution of the bond length distribution within the laser pulse is intensity dependent.

The partially sequential dissociation of carbon dioxide is discussed in terms of the two possible critical distances involved in the carbon dioxide molecule.

Following the initial field ionization of carbon dioxide to $\text{CO}_2^+$, the molecular ion begins to dissociate into $\text{CO}_2^+ \rightarrow \text{CO}^+ + \text{O}$, the $(1,0)$ channel. At this point, two possible channels exist.

(a) The $\text{CO}^+ + \text{O}$ system may dissociate through a critical separation, leading to $\text{CO}^+ + \text{O} \rightarrow \text{CO}^+ + \text{O}^+$, as observed in the covariance mapping experiment.

(b) The carbon monoxide ion may pass through a critical separation, leading to $\text{CO}^+$
\[ \rightarrow C^+ + O^+ . \]

If (a) happens before (b), the (1,1,1) channel will result. Now if we consider the intensity dependence of these two processes, it is clear how the bond length distribution narrows with increasing channel. In low intensity regions, there may be a considerable time separation between the two processes, leading to asymmetric bond extension. In regions of higher intensity, the time separation of these processes will be a great deal smaller. In regions of highest intensity, the two processes will occur at effectively the same time, hence the two bonds will be of almost identical lengths. Molecules in the highest intensity regions will then go on to explode into the highest channels. If only (b) occurs, i.e. if the final reaction is \( \text{CO}_2^{2+} \rightarrow O^+ + C^+ + O \), the carbon ions will be emitted along the laser polarization direction, in accordance with figure 5.15.

5.12 Discussion of simulation results - enhanced ionization

We now return to the results from Cornaggia 1996 and Hishikawa et al 1999 as discussed in chapter 1. In figure 5.23 a comparison is made between the results from the present work and those of Hishikawa et al 1999, who found that their uncorrected momentum maps were best reproduced by bond length distributions which both widened and shifted to higher \( r \) with increasing channel. However, in the present work, we have found that the best-fit distribution follows the opposite trend. Cornaggia (1996) the same \( r \) distribution was used to recreate the lower channels, with \( r_{\text{min}} = 1.16 \ \text{Å}, \ r_{\text{pk}} = 2.32 \ \text{Å} \) and \( r_{\text{max}} = 3.48 \ \text{Å} \). These values are similar to those found in the present work, and somewhat different to those in Hishikawa et al 1999. Admittedly, the agreement between the experimental and simulated MRMI maps of Hishikawa et al 1999 is good (compare figures 1.43 and 1.44). However, the increase of the critical separation with increasing ionization channel is a cause for concern. Hishikawa et al 1999 stated that, having modelled the enhanced ionization of carbon dioxide, "each ionization step occurs at larger \( r \) for larger \( z \)." Although quite true for a specific classical trajectory, this is clearly at odds with the overall intensity dependence as shown by the work of Posthumus and co-workers (see section 1.4.2, specifically figure 1.20).

It is possible that Hishikawa et al (1999) tailored their simulations to cause such behaviour in the \( r \) distribution. As discussed in section 4.7 (figures 4.10 to 4.13),

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limiting the $r$ distribution in this manner will have a knock-on effect on the $\theta$ distribution. This will be discussed in section 5.14.

To try to resolve the dynamics of the enhanced ionization of carbon dioxide, a number of theoretical techniques are employed. Firstly, the applicability of the work of Bandrauk and Ruel (1999) is tested, who found that the critical distance in $\text{H}_3^{2+}$ was approximated by the following expression:

$$r_c \approx \frac{5}{2I_p}$$

Equation 5.7

where $I_p$ is the ionization potential in au. The neutral $\text{CO}_2$ molecule has an ionization potential of $I_p = 13.8$ eV (Rabalais et al 1971), which correspond to $I_p = 0.51$ au. Substituting this value into equation 5.7, we find $r_c = 4.95$ au = 2.62 Å. The ionization potential of $\text{CO}_2^+$ is $I_p = 37$ eV (Herzberg 1966), corresponding to $I_p =$
1.36 au. Substituting these values into equation 5.7, \( r_c = 1.84 \text{ au} = 0.98 \text{ Å} \). It would therefore appear that this simple treatment cannot be applied to carbon dioxide, as Coulomb explosion will be initiated from the \( \text{CO}_2^{2+} \) ion at a bond length shorter than the equilibrium separation.

This result is to be expected to some extent, as Bandrauk and co-workers deal exclusively with the ionization of hydrogenic molecules, where each atom may only be ionized once. This allows the authors to apply a rigorous quantum mechanical treatment to a simple system, then make approximations to their results, whereas in the ionisation of triatomics such as carbon dioxide, no such theoretical treatments have been made.

A robust classical treatment of the Coulomb explosion of \( \text{CO}_2 \) is possible using a development of the field ionization Coulomb explosion of Posthumus et al (1995, 1996a,b). The original diatomic model has been discussed in detail in chapter 1, and has proven to produce results is good agreement with experimental observations. Goodworth (2002) has recently extended the field ionization Coulomb explosion model to the triatomic case. As discussed earlier (section 5.3) the Coulomb explosion of triatomics is considerably more complex as compared to the diatomic case, as the number of possible channels is far greater, and the molecule has an extra degree of freedom in the bending motion. Given the fact that the molecule need not be linear, the laser-molecule potential is treated two dimensionally, and the active electron is allowed to leave in any direction in the plane of the molecule. This model will be discussed fully in Goodworth 2002, hence only the salient points are included here.

As in the diatomic case, the internuclear separation is varied, and the minimum intensity required to produce ionization (appearance intensity) is calculated. The so-called appearance intensity curves for the \((1,1,1)\), \((2,2,2)\) and \((3,3,3)\) channels for carbon dioxide were calculated for a bend angle of 171°, and are shown in figure 5.24.

Clearly simulating only three out of around eleven possible channels is a dramatic simplification. However, it was felt this model could give a useful insight into the mechanics of the ionization. The appearance curves shown in figure 5.24 show minima between \( r = 5.4 \text{ au} = 2.9 \text{ Å} \) \((1,1,1)\) and \( r = 7.5 = 4 \text{ Å} \) \((3,3,3)\). However, the appearance curves do not fully describe the ionization. Rather, the expansion of the molecule within the laser pulse has to be taken into account in a classical trajectory calculation (Posthumus et al 1996, and section 1.4.2.3). The \( \text{CO}_2^{2+} \) ion starts at an
Figure 5.24. Classical appearance intensities of three of the major Coulomb explosion channels of carbon dioxide, indicated by (1,1,1), (2,2,2) and (3,3,3). Also shown are six classical trajectories corresponding to the minimum and maximum intensities necessary to generate the channels.

As the molecule expands, the intensity at time \( t \) is compared to the intensity of the laser pulse, which is given by \( E(t) = E_0 \sin^2 (2\pi t/T) \) where \( T \) is the duration of the laser pulse and \( E_0 \) is the peak intensity. The laser pulse intensity is then plotted as a function of internuclear separation. When this trajectory crosses one of the appearance curves, the charge on each of the ions is increased. Hence, when the trajectory of the \( \text{CO}_2^{2+} \) ion crosses the (1,1,1) appearance curve, the charge on the atoms is increase from 0.66 au to 1 au. Clearly the trajectories must start from a physically justified point - this is chosen to be the appearance intensity of \( \text{CO}_2^{2+} \). The triatomic field ionization model predicted a classical appearance intensity of \( I = 10^{14} \) Wcm\(^{-2} \), corresponding to an electric field of \( E = 0.05 \) au. Hering and Cornaggia (1999) reported an appearance intensity of the \( \text{CO}^+ + \text{O}^+ \) channel between \( 10^{14} \) and \( 2 \times 10^{14} \) Wcm\(^{-2} \), in good agreement with this calculation.

The results of trajectory calculations for a number of peak intensities are shown in
figure 5.24, ranging from just above the appearance intensity of CO$_2^{2+}$ (E = 0.064 au) to the maximum intensity generated (E = 0.923 au). The intensities in figure 5.25 were chosen to reflect the transitions between channels.

The results from the triatomic field ionization model are summarised in table 5.3 below. Comparing the results shown in table 5.3 with the results of the Monte Carlo simulation (figure 5.18 and 5.23), the agreement is good, as the range of critical separations are all within the limits of the simulation results. Therefore, the enhanced ionization model describes the laser-CO$_2$ reaction well.

Table 5.3. Maximum and minimum critical separations, kinetic energy releases and momenta of the oxygen ions as predicted by the triatomic field ionization model.

<table>
<thead>
<tr>
<th>Channel (au)</th>
<th>r (au)</th>
<th>KER (eV)</th>
<th>Exp. KER (eV)</th>
<th>Exp. Mom (10$^3$ amu ms$^{-1}$) of the O$^+$ ion (q = 1,2,3)</th>
<th>Range of exp. mom. (10$^3$ amu ms$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,1,1)</td>
<td>3 (5.4)</td>
<td>12.4 (22.5)</td>
<td>18</td>
<td>117 (131)</td>
<td>100 (300)</td>
</tr>
<tr>
<td>(2,2,2)</td>
<td>4.4 (5.9)</td>
<td>46.5 (60)</td>
<td>70</td>
<td>189 (215)</td>
<td>250 (400)</td>
</tr>
<tr>
<td>(3,3,3)</td>
<td>2.9 (5.3)</td>
<td>115 (216)</td>
<td>116</td>
<td>298 (407)</td>
<td>350 (550)</td>
</tr>
</tbody>
</table>

[a] Measured from the corrected O$^+$ (q = 1,2,3) IMI maps presented in figure 5.12

Also shown in table 5.3 is a comparison between the KER and momentum that would be generated were the molecule to explode from the calculated critical separations. The KER was calculated using equation 5.2, and the momentum was calculated using momentum $p = (mE)^{1/2}$. Comparing the calculated and experimentally observed results, the agreement is reasonable. The agreement is not exact, with the experimental results covering a wider range. However, this is to be expected, following the reduction in the number of ionization channels present in the model.

In general, by comparing the calculated critical separations (triatomic field ionization Coulomb explosion model) with the Monte Carlo results, it can be seen that the triatomic field ionization model predicts values around the peak of the best-fit bond length distributions. The agreement is not exact, but the agreement between the triatomic field ionization model and the Monte Carlo simulation is better than the agreement between either of these results and those of Hishikawa et al 1999.

5.13 Discussion of simulation results - laser-induced reorientation

The results of sections 5.4 and 5.9 indicate that carbon dioxide is reorientated to some extent. To quantify this behaviour, we return to the analysis of Bandrauk and Ruel (1999), who treated the H$_3^{2+}$ ion as a rigid rotor. The rotation period $T_{re}$ of a
rigid molecule with an anisotropic molecular polarizability $\alpha$ and moment of inertia $M$ in an electric field of strength $E_0$ is given by:

$$T_{re} = \frac{\pi}{2} \left( \frac{E_0^2 \alpha}{2M} \right)^{1/2}$$  \hspace{1cm} \text{Equation 5.3}$$

where, in the case of carbon dioxide, $\alpha = 16.6$ au (Guerreiro et al 1997), $M = 2.84 \times 10^5$ au, and $E_0 = 0.923$ au. The moment of inertia of the molecule is estimated by treating the molecule as linear, with equal bond lengths ($r = 1.16 \text{Å} = 2.2$ au). Importantly, the moment of inertia is calculated in terms of the electron mass, as the electric field of the laser drives the electron cloud, which is coupled to the nuclei. Substituting the values above into equation 5.3, we find the period of the reorientation motion to $T_{re} = 315$ au = 7.5 fs.

This value indicates that some of the molecules within the focus will be reorientated within the laser pulse, however it is only a first order approximation. A more quantitative analysis is possible by allowing the electric field of the pulse to vary with time, and by allowing different initial angles to the laser field.

The classical equation of motion of the molecule in the field is given by:

$$\frac{d^2 \phi}{dt^2} = -\frac{E^2(t)}{2} \left( \frac{\alpha}{M} \right) \sin 2\phi$$  \hspace{1cm} \text{Equation 5.4}$$

where $\phi$ is the angle between the O-O axis and the electric field direction and $E(t) = E_0 \sin^2(2\pi t/T)$ is the pulse envelope, where $T$ is the pulse duration in au. The behaviour of the molecule in the field is then simulated by calculating the angular frequency $\omega$ and amount of rotation of the molecule $\Delta \phi$ using the following expressions:

$$\omega_f = \omega_i + \frac{d^2 \phi}{dt^2} \Delta t$$  \hspace{1cm} \text{Equation 5.5}$$

$$\Delta \phi = \omega_i \Delta t + \frac{d^2 \phi (\Delta t)^2}{2}$$  \hspace{1cm} \text{Equation 5.6}$$

where $\Delta t = 0.1$ au and $\omega_i$ and $\omega_f$ are angular frequencies at the beginning and end of the time step. The parameters $\omega$ and $\phi$ are then iterated.

Figure 5.25(a) shows the result of starting the molecule at $\phi = 60^\circ$ to a field of $E = 0.923$ au. As the pulse increases in strength, the molecule is pulled towards the field direction, then oscillates around the field a number of times, then as the field falls in strength, the molecule rotates freely, indicated by the linear portion to
Figure 5.25 Calculation of reorientation of carbon dioxide in a 55 fs pulse focussed to generate an intensity of 0.923 au ($3 \times 10^{18} \text{ Wcm}^{-2}$), initially at 60° to the electric field.

the right of figure 5.25(a).

This technique allows us to calculate the component of the laser field along the internuclear axis. This is shown in figure 5.25(b), where the solid line shows the pulse envelope, and the dashed line shows the axial component of the field. These calculations lead to an important observation, that molecules at an initial angle greater than angular acceptance of the detector (~ 10°) may be reorientated into the detector acceptance within the rising edge of the laser pulse. To investigate this further, a series of calculations were performed at a range of field strengths and initial angles to the field. These results are shown in figure 5.26, where the variation of the axial component of the electric field is plotted as a function of starting angle (y axis) and time (x axis). In each case, the ten greyscale levels are equally spaced between the peak electric field and $E = 0$ au. Figure 5.26(a) and (b) show that molecules near the centre of the focus experience a strong axial field, almost independent of initial angle, indicating reorientation is strong. In the case of
molecules in intermediate regions of the focus (figure 5.26(c) to (f)) there is a considerable drop in the axial field experienced by molecules at angles $\varphi > 60^\circ$, and for molecules in fields $E_0 < 0.1$ au, the axial field is effectively the $\cos (\varphi)$ component, indicating a negligible amount of reorientation.

These calculations have shown that reorientation of carbon dioxide is possible within the laser pulse. This treatment does not explain why ions that explode into the (1,1,1) channel are reorientated most strongly. This will be returned to in section 5.15.

It should be pointed out that these calculations only deal with the neutral CO$_2$ molecule - no allowance has been made for any expansion of the molecule, which will change the moment of inertia and polarizability. Furthermore no ionization takes place, which is dependent on the field along the internuclear axis, and ionizing the molecule will alter the rate at which the bond expansions take place.

5.14 Discussion of simulation results - bend angle evolution

A number of bend angle distributions of carbon dioxide are shown in figure 5.27 (Sanderson et al 1999b, Cornaggia 1996 and Hishikawa et al 1999), along with the zero-point distribution (Herzberg 1966). The results in figure 5.27 are ordered from top to bottom in increasing molecule-field interaction time, starting at zero (Herzberg
1966), 6 fs in the case of 120 keV Ar\(^{8+}\) ions (Sanderson et al. 1999b), 55 fs in the present work, 100 fs laser pulses (Hishikawa et al. 1999) and 130 fs laser pulses (Cornaggia 1996).

Two distinct types of behaviour can be seen in figure 5.27. In figures 5.27 (a) to (c), the bend angle distributions begin between 145° and 160°, peak between 170° and 175°, and fall towards zero at 180°. The distributions in figures 5.27(d) and (e) however peak at 180°, and fall to zero between 125° and 145°.

By making a linear approximation to the distributions of Hishikawa et al. 1999, the differences in the bend angle distributions may be understood in terms of a physical effect and an instrumental effect.

![Figure 5.27. Comparison between the bend angle distributions for carbon dioxide under a range of different field conditions. (a) Zero-point distribution. (b) HCI impact with a molecule-field interaction time of 6 fs. (c) Present work with 55 fs laser pulses. (d) 100 fs laser pulses with linear approximation (dashed lines) and (e) 130 fs laser pulses.](image-url)
The physical effect is an apparent broadening of the bend angle distribution with increasing molecule-field interaction time. This observation is based on an increase in the angle at which the bend angle falls to zero increasing from ~ 160° (figure 5.27a) to 140° (figure 5.27c).

The result of the instrumental effect is present in the distributions of Hishikawa et al 1999 and Cornaggia 1996, where the authors have not applied a transmission correction, hence as discussed earlier, low energy ions will be detected preferentially. In Sanderson et al 1999b, there is no instrumental effect, as the bend angle distribution is measured directly, and in the present work, the instrumental effect has been removed.

Focussing on the results of Hishikawa et al 1999, the apparent narrowing of the bend angle distribution with increasing z, it is suggested that this is a consequence of constraints applied to the simulation process (as discussed in section 5.12). For the low z channels (averaged into the z = 3 distribution), the authors may have underestimated the width and position of the bond length distribution, resulting in overly energetic oxygen ions. By increasing the width of the bend angle distribution, this effect may be compensated for. As discussed in section 4.7, this broadening will cause the carbon ions to gain momentum perpendicular to the O-O axis. However, as the peak in the carbon ions is at zero momentum, the effect of the broadening the bend angle distribution will be in the wings of the simulated carbon ions.

The agreement between the present bond length distributions and those of Hishikawa et al 1999 improves as z increases (see figure 5.23), hence we would expect the agreement between the width of the bend angle distribution to improve. As can be seen in figure 5.27, this argument holds true. It therefore appears that the present result (one bend angle distribution to represent all channels) is reasonable.

Following the results of the Monte Carlo simulation of the Coulomb explosion of carbon dioxide, a straightforward observation may be made. As all of the three-body Coulomb channels may be reproduced by the same bend angle distribution, it appears that, if this process is occurring, it occurs before the molecule begins to explode. Therefore, following the discussion on partially sequential dissociation above, this process must occur either in the neutral molecule or the singularly and doubly charged molecular ions.

To explain the change in the bend angle distribution (compare figures 5.15 and 5.19),
we initially turn to the principle of light-dressed potentials (see chapter 4 and Sanderson et al 1999b for application to water, Hishikawa et al 1999 for simplified application to carbon dioxide and Guisti-Suzor et al 1995 and chapter 1 for general discussion), which modify the electronic structure of the molecule such that geometry modifications occur.

Figure 5.28(a) shows the ground state of CO$_2$ ($^1 \Sigma_g^-$ state 1 in figure 5.28(a)) along with a number of excited electronic states taken from Rabalais et al 1971. The laser wavelength of 790 nm is equivalent to a photon energy of 1.6 eV, therefore states 2 to 5 on figure 5.28(a) may be accessed by three-photon excitation (4.8 eV), and states 6 and 7 may be accessed by six-photon excitation (9.6 eV).

Figure 5.28(b) illustrates the effect of dressing states 2 and 3 by three photons. States 4 and 5 have not been included, as the ground state does not intersect these states until around 2 eV. Consequentially, transfer of the vibrational population from the ground state to either dressed state is not possible at room temperature.

We now examine how the dressed potentials would allow the bend angle distribution to evolve qualitatively. In figure 5.28(b), state 3 is the most favourable three photon dressed state, as the crossing occurs around 160°, and the ground state vibrational

\[ \begin{align*}
7 &= ^1 \Pi_g (^\Delta_g) \\
6 &= ^1 \Pi_u (^\Sigma_u) \\
5 &= ^1 \Sigma_+ (^\Sigma_u) \\
4 &= ^1 \Delta_u (^\Pi_g) \\
3 &= ^1 \Sigma_+ (^\Delta_u) \\
2 &= ^1 \Delta_g (^\Pi_u) \\
1 &= ^1 \Sigma_g^- (^\Sigma_u) 
\end{align*} \]
population would be able to cross to this state through the avoided crossing (blue dashed line). This crossing would cause the peak of the bend angle distribution to shift to higher angles, in the range $130^\circ < \theta < 160^\circ$, and we would expect the distribution to fall to zero at $\theta = 180^\circ$. State 2 dressed by three photons appears not to agree with the results of the Monte Carlo simulation, as the vibrational population would cross from the ground state to state $2 - 3h\nu$, and fall into the minimum around $130^\circ$. This would shift the peak in the bend angle distribution to a similar angle.

The six photon dressing of state 7 does not cross the ground state bending potential curve, hence, in this simple picture, here cannot be any population transfer. State 6 dressed by six photons however does cross the ground state, and like state $3 - 3h\nu$, appears to support a bend angle agreement similar to that seen in the Monte Carlo simulations. Transfer of population into this state would cause a broadening of the bend angle distribution out to $\theta = 145^\circ$, and the peak of the distribution would shift to lower angles.

Importantly, it appears it is possible to explain the simulation results through dressing of the linear ground state by a broad yet linear (state $6 - 6h\nu$) or nearly linear (state $3 - 3h\nu$) potential energy curve.

The work of Hochlaf et al (1998) provides an alternative mechanism for the evolution of the bend angle distribution. Hochlaf and co-workers used an \textit{ab initio} technique to examine the electronic states of CO$_2^{2+}$, and to do so calculated a potential energy function (PEF) for the ground state of the molecular ion. Figure 5.29 shows the PEF for the ground state of CO$_2$ (solid line) and CO$_2^{2+}$ (dashed line). The horizontal red line represents the extent of the linear approximation to the zero point motion of CO$_2$ (see figure 5.15), hence the vertical red arrow illustrates the range of angles through which the molecule oscillates on this surface. As can be seen, the lower end of this arrow almost intersects the third contour of the CO$_2$ PEF, corresponding to an energy of 1500 cm$^{-1}$. If we then assume that this vibrational population still exists in the CO$_2^{2+}$ ion, it appears that the molecular ion will oscillate over a very similar range to that predicted by the simulation results. The horizontal blue line on figure 5.29 corresponds to an energy of 1500 cm$^{-1}$ on the CO$_2^{2+}$ PEF, and the blue arrow indicates the range of bends possible.

This argument is given further credence by estimating the point of the CO$_2$ PEF which corresponds with the peak in the zero point distribution (black square on
Figure 5.29. Ground state potential energy surfaces for CO$_2$ (solid line) and CO$_2^{2+}$ (dashed line) taken from Hochlaf et al 1998. In both cases, the contours are separated by 500 cm$^{-1}$. The red arrow indicates the extent of the zero point bending motion. The blue arrow indicates the extent of the bending motion of the CO$_2^{2+}$ ion assuming direct population transfer.

figure 5.29). If this point is transferred to the CO$_2^{2+}$ PEF (black circle), it appears that a value of $\theta_{pk} \approx 170^\circ$ is expected, and a range of $154^\circ < \theta < 180^\circ$. Comparing these values with figure 5.19, there is strong agreement. Furthermore, bearing in mind CO$_2^{2+}$ is observed in the present experiment, whereas three- and six-photon dressing is only hypothesised, the bend angle distribution therefore appears to be modified during the first two stages of ionization to reflect the natural bending motion of the CO$_2^{2+}$ ion.

Despite being a simple treatment, this idea is corroborated by two major points. Firstly, it explains the experimental observations well. Secondly, the behaviour of the CO$_2^{2+}$ ion has been shown to be very influential in both laser-induced reorientation and enhanced ionization. It is expected that these two processes are strongly coupled to the modification of the geometry of the exploding molecule.

With reference to the work of Cornaggia (1996), because of the necessity for a wide angular acceptance, covariance mapping is not as well suited to studying the bending motion in triatomics as either the current IMI + Monte Carlo technique or the MRMI
technique of Hishikawa and co-workers. However, both Cornaggia et al 1995 and Cornaggia 1996 are valuable contributions to the field of laser-molecule interactions.

5.15 Discussion of results - competition of enhanced ionization and laser-induced reorientation in the Coulomb explosion of CO₂

It has been shown that laser-induced reorientation can occur within the laser pulse. However, as yet, the mechanism causing reorientation to be maximised for the (1,1,1) channel has not been discussed (section 5.4).

Assuming that the reorientation model is a reasonable representation of the system, and also assuming that energetic ions which reach the detector originate from a small angle around the polarization direction, the maximum observed in figure 5.6 may be explained by coupling the enhanced ionization model (section 5.12) with the reorientation model (section 5.13). As shown in figure 5.24, the pulse profile experienced by the molecule dictates which Coulomb channels are accessed. Furthermore, as shown in figure 5.25, the reorientation process has a strong influence on the field along the O-O axis.

If we now consider the fate of molecules in a range of different orientation and field conditions, it becomes clear why reorientation is maximised for the lowest three-body channel. In this discussion, only the (1,1,1), (2,2,2) and (3,3,3) channels have been considered. The overall behaviour is summarised in the following table.

<table>
<thead>
<tr>
<th>Intensity</th>
<th>Alignment</th>
<th>Final channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>High</td>
<td>(1,1,1)</td>
</tr>
<tr>
<td>Low</td>
<td>Low</td>
<td>None</td>
</tr>
<tr>
<td>Med</td>
<td>High</td>
<td>(2,2,2)</td>
</tr>
<tr>
<td>Med</td>
<td>Med</td>
<td>(1,1,1)</td>
</tr>
<tr>
<td>Med</td>
<td>Low</td>
<td>None</td>
</tr>
<tr>
<td>High</td>
<td>High</td>
<td>(3,3,3)</td>
</tr>
<tr>
<td>High</td>
<td>Med</td>
<td>(2,2,2)</td>
</tr>
<tr>
<td>High</td>
<td>Low</td>
<td>(1,1,1)</td>
</tr>
</tbody>
</table>

Put simply, over the range of intensities present in the focus, more molecules will Coulomb explode into the (1,1,1) channel, as this channel may be generated over a wider range of alignment-intensity combinations. The interplay between the reorientation and enhanced ionization mechanisms causes misaligned molecules to experience a low initial effective field, then the reorientation process increases this effective field, and the final channel depends on the maximum field along the
molecular axis. The effect of the reorientation process is to increase the field experienced by the molecule, then the enhanced ionization process effectively stops reorientation and ionises the molecule.

5.16 Summary
The covariance mapping technique was used to investigate the kinetic energy release in the Coulomb explosion of CO$_2$. Comparisons were made with other experimental observations at different molecule-field interaction times. An overall decrease in the bond length at which explosion occurred was observed with decreasing pulse length, in accordance with the field-ionization Coulomb explosion model. A simple one-dimensional time-of-flight comparison technique was used to investigate the reorientation of CO$_2$. Circular and linear laser pulses are used, where the laser electric field component of both pulses was identical in the direction of the detector. It was found that the laser pulse reorientated all ionization stages of CO$_2$, and that this process was strongest for the lowest three-body Coulomb channel. Finally, the ion momentum imaging and Monte Carlo techniques were used to quantify the geometry of the exploding molecule. The best-fit simulation results indicated that the bond length distribution peaked at around double the equilibrium separation, and narrowed with increasing explosion channel. This observation was explained using a triatomic field ionization model. The reorientation of CO$_2$ was investigated by simulating the interaction of the induced dipole moment with the laser electric field, and it was found that CO$_2$ was heavily influenced by the electric field present. The maximisation of the reorientation process was explained qualitatively by examining the competition between enhanced ionization and reorientation. It was concluded that reorientation increased the number of molecules aligned with the field, and the explosion of the molecule effectively stopped reorientation. The best-fit bend angle distribution was observed to broaden and peak at a larger angle as compared to the expected ground state distribution. This broadening was qualitatively explained by multiphoton dressing of the excited states of CO$_2$. However, it was also found that the geometry of the CO$_2^{2+}$ molecular ion described this observation.
Chapter 6. Conclusion and suggestions for future research

Conclusion

The interaction of 55 fs 790 nm titanium: sapphire laser pulses focused to $3 \times 10^{16}$ Wcm$^{-2}$ with H$_2$O and CO$_2$ has been investigated using three experimental techniques based on time-of-flight mass spectroscopy. This work has demonstrated a new ion imaging technique, used to quantify the geometry of Coulomb exploding triatomic molecules, through a correction procedure and Monte Carlo simulation. As discussed above, this technique has allowed us to examine the explosion process in detail. A linear-circular polarization comparison technique, originally applied to diatomics, has been applied to a triatomic for the first time, and covariance mapping has been applied and comparisons made with earlier results.

In both CO$_2$ and H$_2$O, the electric field strength generated by the laser pulses caused rapid multiple ionization, leading to Coulomb explosion into three atomic ions. Three major processes have been observed in the laser-molecule interaction within the pulse duration: enhanced ionization at a critical separation, laser-induced reorientation and bend-angle modification. That the field ionization Coulomb explosion model describes the laser-molecule interaction indicates that the interplay between the laser and Coulomb fields and the atomic ionization potentials is a good description of the ionization mechanics. Laser-induced reorientation has been simulated, and it appears that the coupling between the laser electric field and the molecular polarizability describes the system qualitatively. A number of mechanisms have been proposed to account for the evolution of the bend angle distribution. In the case of both molecules, the stability and geometry of the molecular ion before and during Coulomb explosion is pivotal to the dynamics of the explosion.

Suggestions for future research

Research into laser pulse generation and amplification techniques will bring increasing repetition rates, shorter pulse durations and higher pulse energies. Increasing repetition rates bring a clear advantage, especially in the case of coincidence or covariance experiments. Shorter pulses and higher pulse energies will
generate far higher intensities, allowing the exposure of matter to even higher
electric field strengths. Specifically, the majority of the ionization dynamics occurs
within the rising edge of the pulse, hence a faster rise time could temporally resolve
the processes observed.

In the immediate future, the best candidate for decreasing pulse duration is
generating few-cycle pulses employing hollow-waveguides (Nisoli et al 1996) or
ultra-broadband chirped mirrors (Nisoli et al 1997) for the compression of
Ti:sapphire pulses. Recently, high repetition rate systems have been demonstrated
which deliver pulse energies 3 - 5 mJ with pulse durations of ~20 fs (Backus et al
1995).

To resolve molecular processes that occur on the femtosecond time scale, it would be
a clear advantage to be able to employ sub-femtosecond laser pulses. To this end,
attosecond pulse generation is currently under intense investigation. A number of
groups have proposed mechanisms for the production of x-ray bursts hundreds of
attoseconds in duration (summarised in Brabec and Krausz 2000), mainly concerned
with high harmonic generation. Interestingly, a recent publication by Numico et al
(1999) proposed a mechanism for generating attosecond pulse trains from the high-
order harmonics generated after the photo-dissociation of the hydrogen molecular
ion. This is of particular relevance, as we have recently studied the dissociation and
Coulomb explosion of the hydrogen molecular ion in an intense laser field for the
first time (appendix A7.8, Williams et al 2000).

Whatever the mechanism, it seems certain that laser pulses available to
experimentalists will decrease in length and increase in energy. The immediate
advantage of such pulses is the ability to temporally resolve the processes under
investigation in the present work. By employing pump-probe techniques, combining
sub-femtosecond pulses with pulses of the order of 50 fs may allow us to directly
observe the expansion, reorientation and geometry modification of the molecules
within the longer pulse.

Another exciting possibility is to use a tunable dye laser to excite specific transitions
in the molecule in question. Using this technique, it may be possible to initiate a
chemical reaction, then to directly image the progress of the reaction through
temporal control of the Coulomb explosion of the system.

The control of chemical processes could be taken one step further using coherent
control (Judson and Rabitz 1992), which employs an experimental feedback loop to
maximise a particular process. Very recently, Pearson et al (2001) successfully demonstrated the application of adaptive learning algorithms to coherent control. In terms of data collection, the need for the correction function and simulation process could be removed by employing a position- and time-sensitive detector as recently demonstrated by Sanderson et al (1999b). This type of system would allow the direct measurement of the momentum vectors of the ions, rather than the momentum component in the case of the present spectrometer. A number of different detector types exist, hence it would be necessary to assess which would be best suited to studying the explosion of polyatomic molecules.

The application of these proposed techniques would lead to an advance in understanding in this field. However, without the complementary theoretical studies, the importance of these observations will be somewhat limited. As discussed in chapter 1 of this thesis, full quantum mechanical models of laser-molecule interactions are currently only capable of dealing with simple hydrogenic molecules. It is expected however, that these studies will pave the way for future researchers to simulate the behaviour of the systems investigated in the present work.

By coupling a number, if not all, of these suggestions, it is felt that this fascinating field of research may be further advanced.
Appendix 1. Detector schematic

Key.
1 Anode connector
2 Copper anode
3 PTFE insulating washer
4 Copper contact to upper face of MCP2
5 Micro-channel plate 2 (MCP2)
6 Copper contact between MCP1 and MCP2
7 Micro-channel plate 1 (MCP1)
8 Copper contact to lower face of MCP1
9 Collection grid on copper washer
10 Stainless Steel insert
11 Copper aperture
12 Drift tube
Appendix 2. Equations of motion for time-of-flight mass spectrometer

\[ u_y = \left( \frac{pm_y}{m} \right) \cos \left( \frac{\pi \theta}{180} \right) \]  
\[ t_T = \frac{m}{q e_1} \left[ -u_y + \sqrt{u_y^2 + \frac{2q e_1 s_1}{m}} \right] \]  
\[ t_A = \frac{m}{q e_2} \frac{\sqrt{-u_y^2 + \frac{2q e_1 s_1}{m} + \frac{2q e_2 s_2}{m}}}{\sqrt{m}} \]  
\[ t_D = \frac{s_3}{v_{Ay}} \]  
\[ v_{Ty} = \sqrt{u_y^2 + \frac{2q e_1 s_1}{m}} \]  
\[ v_{Ay} = \sqrt{u^2 + \frac{2q e_1 s_1}{m} + \frac{2q e_2 s_2}{m}} \]  
\[ t_{total} = t_T + t_A + t_D \]

where

- \( q \) is ion charge (au)
- \( m \) is ion mass in (amu),
- \( \theta \) is the initial direction of the ion with respect to the spectrometer axis (degrees)
- \( e_1 \) is the extraction field strength (Vm\(^{-1}\))
- \( e_2 \) is the acceleration field strength (Vm\(^{-1}\))
- \( s_1 \) is the distance from the source region of the TOFMS to the top plate (m)
- \( s_2 \) is the distance from the top plate to the acceleration grid (m)
- \( s_3 \) is the distance from the acceleration grid to the end of the drift tube (m)
- \( u_y \) is the component of the initial velocity of the ion perpendicular to the spectrometer axis (ms\(^{-1}\))
- \( t_T \) is the time-of-flight between the interaction region and the top plate (s)
- \( t_d \) is the time-of-flight between the top plate and the acceleration grid (s)
\( t_D \) is the time of flight along the drift tube (s)
\( t_{\text{total}} \) is the total flight time from the interaction region to the grid/aperture at the end of the flight tube (s)
\( v_{TY} \) is the velocity of the ion perpendicular to the spectrometer axis on arriving at the top plate (ms\(^{-1}\))
\( v_{AY} \) is the velocity of the ion perpendicular to the spectrometer on arriving at the acceleration grid (ms\(^{-1}\))

**Conversion of time-of-flight to ion kinetic energy and momentum**

For an ion of charge \( q \), with mass \( m \), produced in an extraction field \( \varepsilon \) (variable \( \varepsilon_i \) in equations A2.2 to A2.6), has a kinetic energy \( K_E \) and momentum \( p \). Momentum and kinetic energy are related to the difference in the flight time of the ion from the zero-momentum position, \( \Delta t \) by:

\[
p(\Delta t) = k q e \Delta t \quad \text{Equation A2.8}
\]

\[
K_E(\Delta t) = \frac{a (q e \Delta t)^2}{m} \quad \text{Equation A2.9}
\]

where

- \( q \) is ion charge in (au)
- \( m \) is ion mass in (amu)
- \( \varepsilon \) is the extraction field strength in (Vm\(^{-1}\))
- \( \Delta t \) is the difference between the ion time-of-flight of the ion and the zero-momentum time-of-flight (s)

\( k = 9.824 \times 10^9 \)

\( a = 5 \times 10^{11} \)

These equations generate \( p \) in amu ms\(^{-1}\), and \( K_E \) in eV.
Appendix 3. Tektronix TDS 744A specifications

Summary

- InstaVu™ Acquisition (up to 400,000 wfms/sec)
- 500 MHz bandwidth (TDS 754A/744A/724A);
  1 GHz (TDS 784A/782A)
- Sample rates to 2 GS/s (TDS 782A/754A/744A);
  1 GS/s (TDS 724A)
  4 GS/s (TDS 784A)
- 2 input channels (TDS 782A/724A);
- 4 input channels (TDS 784A/754A/744A)
- Pulse width, 1 ns glitch; runt, pattern, state, triggering
- 1 mV/div to 10 V/div sensitivity
- Infinite and variable persistence
- Color Grading
- Record lengths to 500,000 points (250,000 points on TDS 782A/724A)
- 8-bit vertical resolution and up to 13 bits with HiRes
- High resolution color monitor
- 3.5 inch DOS floppy disk drive (standard)
- Vertical accuracy to 1%
- Tek TriStar™ (DSP) processor
- Slew Rate, Setup & Hold Violation, and Time-out triggers
- Waveform pass/fail testing
- Advanced signal processing functions
- 25 automatic measurements
- Full GPIB programmability
- Desktop publishing outputs
- HDTV Video trigger option
- Segmentable acquisition memory
- VGA output
- 3 year warranty
- Direct Readout in "Amperes" and "Watts" using P5200 and TCP202 Probes
- Channel Deskew
- HP Deskjet printer support

Characteristics

Channels: 4 (2 Channels for TDS 782A/724A)
Samplers: 4 (2 Channels for TDS 782A/724A)
Bandwidth*:
  1 GHz ** (TDS 784A/782A)
  500 MHz*** (TDS 754A/744A)
  500 MHz (TDS 724A)

* Reduce the upper bandwidth frequencies by 2.5 MHz for each degree C above 30 degree C.

** 50 ohm; 1 mV/div: 500 MHz, 2 mV/div: 600 MHz, 5 mV/div: 900 MHz. Reduce the upperbandwidth frequencies by 5 MHz for each degree C above 30 degree C.

*** 1 mV/div: 450 MHz.

Sensitivity

CH1, CH2: 1 mV to 10 V/div
CH3, CH4: 1 mV to 10 V/div
Position Range: +/-5 Divisions.
Offset

CH1, CH2:
+/-1 V from 1 mV to 100 mV/div (TDS 784A/782A)
+/-1 V from 1 to 99.5 mV/div (TDS 754A/744A/724A)

AUX 1, AUX 2:
+/-10 V from 101 mV to 1 V/div, +/-100 V from 1.01 V to 10 V/div

CH3, CH4:
+/-1 V from 1 to 99.5 mV/div

Maximum Sample Rate

Any One Channel:
2 GS/s (TDS 782A/754A/744A)

Any Two Channels:
1 GS/s (TDS 744A)

Four Channels:
500 MS/s (TDS 744A)

Three, Four Channels:
500 MS/s (TDS 744A)

Maximum Record Length

Any One Channel:
50K (500K opt.) (TDS 784A/754A/744A)

Any Two Channels:
50K (250K opt.) (TDS 754A/744A)

Any Four Channels:
50K (130K opt.) (TDS 784A/754A/744A)

Any Three, Four Channels:
50K pts (130K w/ Opt. 1M) (TDS 784A/754A/744A)

Time Base System

Time Bases: Main, Delayed.
Time Base Range: 500 ps to 10 s/div. (10,000 s/div with fit-to-screen for TDS 754A/744A/724A)
200 ps to 10 s/div. 4 ps (to 2500 s/div with fit-to-screen or zoom TDS 784A/782A)

Time Base Accuracy (over any interval >/= 1 ms): +/-25 ppm.
Pre-Trigger Position: 0% to 100% of any record.
Delay Between Channels (any 2 channels with equal V/div and coupling): </= 50 ps.

Vertical System

DC Gain Accuracy: +/-1.0% (Warranted); +/-0.7% (Typical).
Vertical Resolution: 8 bits (256 levels over 10.24 vertical divisions). >/=13 bits with HiRes; >/=11 bits with averaging.
Analog Bandwidth Selections: 20 MHz, 250 MHz, and full.
Step Response Setting: </=0.5% error within 20 ns of a </=2 V step.
Effective Bits:
5.5 Bits (1 GHz at 4 GS/s) (TDS 784A/782A)
6.8 Bits (500 MHz at 2 GS/s) HiRes. 9.7 Bits (1 MHz at 10 MS/s). (TDS 754A/744A/724A)
9.7 Bits with HiRes (1 MHz at 10 MS/s) (TDS 784A/782A)
Input Coupling: AC, DC or GND.
Input Impedance Selections: 1 Megohm in parallel with 10 pF, or 50 ohm (AC and DC coupling).
Maximum Input Voltage: +/-400 V (DC+ peak AC). Derate at 20 dB/decade above 1 MHz. 1 Megohm or GND coupled.
Channel Isolation: >/=100:1 at 100 MHz and >/=30:1 at bandwidth for any two channels having equal Volts/div settings.
AC Coupled Low Frequency Limit: \(\leq 10\) Hz when AC 1 Megohm coupled. \(\leq 200\) kHz when AC 50 ohm coupled.

**Acquisition Modes**

InstaVu™: Instantaneous capture of random anomalies and changing signals. Captures up to a maximum of 400,000 waveforms per second (TDS 784A/754A/744A). Uses color grading to show relative occurrence of events.

Peak Detect: High frequency and random glitch capture. Captures glitches of 1 ns using acquisition hardware at all real-time sampling rates.

Sample: Sample data only.

Envelope: Max/min values acquired over one or more acquisitions.

Average: Waveform averages selectable from 2 to 10,000.

HiRes: Vertical resolution improvement and noise reduction on low-frequency signals, e.g. 13 bits at 50 microsecond/div and slower.

FastFrame™: Acquisition memory size segmentable with trigger rate up to 50,000 per second from 50 to 5,000 points per frame (independent of the number of channels).

Single Sequence: Use Run/Stop button to capture a single triggered acquisition at a time which may be automatically saved to NVRAM with AutoSave.

**Trigger Types**

EDGE (main and delayed): Conventional level driven trigger. Positive or negative slope on any channel or rear panel auxiliary input. Coupling Selections: DC, AC, noise reject, HF reject, LF reject.

PULSE (main):

  - WIDTH: Trigger on width of positive or negative pulse either within or not within selectable time limits. Time limits settable from 1 ns to 1 s.
  - GLITCH: Trigger on or reject glitches of positive, negative or either polarity. Minimum glitch width threshold is 1.0 ns, with 200 ps resolution.
  - RUNT: Trigger on a pulse that crosses one threshold but fails to cross a second threshold before crossing the first again.
  - SLEW RATE: Trigger on pulse edge rates that are either faster or slower than a set rate. Edges can be rising, falling, or either.
  - TIME-OUT: Trigger on an event which remains high, low, or either, for a user-specified time.

LOGIC:

  - PATTERN: Specifies a logical combination (AND, OR, NAND, NOR) of the four input channels (Hi, Lo, Don't Care). Trigger when pattern stays True or False for user specified time.
  - STATE: Any logical pattern of channels 1, 2 and 3 plus clock edge on channel 4. Triggerable on positive or negative clock edge.
  - SETUP & HOLD: Trigger on violations of both setup time and hold time between clock and data which are on separate input channels.

VIDEO (Optional) NTSC, PAL, HDTV, FlexFormat™: Trigger on a particular line of individual, odd/even, or all fields. Trigger on a specific pixel of a line by using video trigger with delay by events. Choose horizontal sync polarity. Choose from popular HDTV formats (1125/60, 1050/60 1250/50, 787.5/60) or use FlexFormat™ for other HDTV-type formats by defining frame rep rate, number of lines and fields, and sync timing structure.

**Triggering System**

Triggers: Main, Delayed.

Main Trigger Modes: Auto, Normal, Single.

Delayed Trigger: Delayed by time, events, or events and time.

Time Delay Range: 16 ns to 250 s.

Events Delay Range: 1 to 9,999,999 events.
**External Rear Input:** \( \geq 1.5 \) kilohm; Max input voltage is \(+/-20\) V (DC + AC peak).

**Display**

**Waveform Style:** Dots, vectors, variable persistence selectable from 250 ms to 10 s, infinite persistence, and intensified samples.

**Color:** Standard palettes and user definable colors for waveforms, text, graticules, and cursors. Measurement text and cursor colors matched to waveform. Waveform collision areas highlighted with different color. Statistical waveform distribution shown with color grading through variable persistence.

**Color Grading:** With variable persistence selected, historical timing information is represented by temperature or spectral color scheme providing "z-axis" information about rapidly changing waveforms.

**Gray Scaling:** With variable persistence selected, waveform points time-decay through 16 levels of intensity.

**Waveform Capture Rate:** For 500 point waveforms with infinite persistence mode selected: 150/sec typically. With InstaVu: up to 400,000/sec (TDS 784A/754A/744A).

**Graticules:** Full, grid, cross hair, frame. NTSC and PAL with video trigger option.

**Format:** YT and XY.

**Fit to Screen:** Entire acquisition memory displayed on screen.

**Measurement System**

**Automatic Waveform Measurements:** Period, Frequency, High, Low, + Width, -Width, Maximum, Minimum, Rise, Fall, Peak to Peak, Amplitude, + Duty cycle, -Duty cycle, + Overshoot, -Overshoot, Propagation Delay, Burst Width, Mean, Cycle Mean, RMS, Cycle RMS, Area, Cycle Area, Phase. Continuous update of up to four measurements on any combination of waveforms.

**Thresholds:** Settable in percentage or voltage.

**Gated:** Any region of the record may be isolated for measurement using vertical bars.

**Snapshot:** Performs all measurements on any one waveform showing results from one instant in time.

**Cursor Measurements:** Absolute, Delta; Volts, Time, Frequency. NTSC IRE and Line Number with video trigger option.

**Time Measurements Accuracy:** (Single Shot Typical)
- <38 ps typical @ 4 GS/s Single Shot (TDS 784A)
- <80 ps @ 2 GS/s Single Shot (TDS 782A/754A/744A)
- <150 ps @ 1 GS/s Single Shot (TDS 724A)

**Cursor Types:** Horizontal bars (volts); Vertical bars (time); operated independently or in tracking mode.

**Computer Interface**

**GPIB (IEEE-488.2) Programmability:** Full talk/listen modes. Control of all modes, settings, and measurements.

**Storage**

**Waveforms:**
- 4 full 50K (with Option IM: 2 full 130K point, 1 full 250K point, or 1 compressed 500K point waveform) (TDS 784A/754A/744A)
- 2 full 50K (with Option IM: 2 full 130K point, 1 full 250K point waveform) (TDS 782A/724A)

**Setups:** 10 front panel setups.

**Floppy Drive:** Store reference waveforms, setups, (and data files w/TDS 784A) and image files on 3.5 inch 1.44 MByte or 720 KByte DOS format floppy disk.

**CRT**

**Type:** 7 in. diagonal, NuColor™ liquid crystal full color shutter display. 256 color levels.

**Resolution:** 640 horizontal by 480 vertical displayed pixels (VGA).
Appendix 4. LabVIEW software and documentation

The following appendix is intended to give the reader an understanding of the software developed as part of this research. Instead of presenting all the LabVIEW diagrams, which requires the reader to learn the language, each VI is broken down into a flowchart. In the case of the largest VIs, designed to control complex aspects of the data collection and processing, the Front panel is presented, followed by a simple hierarchy diagram, indicating overall dataflow.

With reference to the notation used in this appendix, the following terms apply:

'Index' - Read an element or group of elements from an array.

'Size' - Function which measures the number of elements in each dimension of an array,

'Error in' and 'Error out' - A group of variables passed between VI, the value of which indicates whether the VI has executed as expected. In the case of GPIB communications, these functions are used to ensure sequential execution.

'Shift registers' - Applicable to For and While loops. Shift registers pass the output from one iteration of a loop to the next.

'Sequence structure' - A LabVIEW function which controls the order of execution of a VI. The sequence structure is layered, such that each layer is executed once, and in a predefined order.
Flowchart Key

**TERMINATOR**
Used to start or stop a flow diagram.

**PROCESS**
Used to perform a calculation or to process inputs.

**DECISION**
Selects which of the following sections of the flow diagram are performed, depending on a Boolean decision.

**DATA IN/OUT**
Used to pass data to and from a flow diagram.

**MANUAL INPUT**
Illustrates when the user interacts with the Virtual Instrument.

**DISPLAY**
Shows when data is passed from the block diagram to the front panel, hence to the PC display.

**PREDEFINED PROCESS**
Shows when a flow diagram calls a subVI, which has been defined earlier in this appendix.

**OFF-PAGE CONNECTOR**
Used when the flow diagram has to operate across two or more pages. The connectors are referenced by the VI name and the section number, along with an identification letter.
List of all variables

- \( t \): time (s)
- \( \Delta t \): time increment (s)
- \( q \): charge (au)
- \( m \): mass (amu)
- \( u \): initial velocity (ms\(^{-1}\))
- \( v \): final velocity (ms\(^{-1}\))
- \( \text{acc}_{1x} \): acceleration of ion 1 in x direction (ms\(^{-2}\))
- \( \text{acc} \): acceleration (ms\(^{-2}\))
- \( \text{p} \): momentum (amu ms\(^{-1}\))
- \( s \): displacement (m)
- \( \Delta s \): displacement increment (m)
- \( \tau \): internuclear bond length (Å)
- \( \theta \): internuclear bond angle (degrees)
- \( \phi \): alignment angle (degrees)
- \( \text{mid}_{1} \): mid-point 1 of r- and θ-distributions
- \( \text{mid}_{2} \): mid-point 2 of r- and θ-distributions
- \( \psi \): angle between \( p \) and electric field (degrees)
- \( \alpha \): angle relative to TOF axis (degrees)
- \( \beta \): angle between laser polarization and TOF axis (degrees)
- \( \rho \): simulation parameters
- \( \epsilon \): correction factor value
- \( \text{ix}, \text{iy} \): general ion co-ordinates (Å)
- \( \text{x}_{1}, \text{y}_{1} \): ion 1 specific co-ordinates (Å)
- \( \text{n}_{a} \): number of angles
- \( \text{n}_{\text{pt}} \): number of points to shift
- \( \text{x}_{\text{dist}}, \text{Y}_{\text{dist}} \): dimensions of MI array
- \( \text{n}_{\text{ch}} \): number of channels in simulation
- \( \text{d} \): ion displacement across detector (m)
- \( \text{n}_{x}, \text{n}_{y} \): dimensions of section of covariance map
- \( T \): time array [1D] (s)
- \( P \): momentum array [1D] (amu ms\(^{-1}\))
- \( \text{P}_{\text{sim}} \): simulated momentum array [2D] (amu ms\(^{-1}\))
- \( E \): kinetic energy (eV)
- \( V \): voltage (V)
- \( D \): all data [3D] (s, V, degrees)
- \( \text{A} \): all angles array [1D] (degrees)
- \( \text{A}_{\text{sim}} \): simulated array of \( \text{A} \) [2D] (degrees)
- \( S \): all ion signal [2D] (V)
- \( \text{D}_{\text{sim}} \): simulated ion signal array [2D]
- \( \text{D}_{\text{ch}}(q) \): simulated ion signal array (quadrant) [2D]
- \( \text{D}_{\text{ch}}(cb) \): simulated ion signal array with \( n_{c} \) channels scaled independently
- \( I \): index of \( D \)
- \( W \): waveform [2D] (s, V)
- \( W_{p} \): filtered waveform [2D] (s, V)
- \( W_{t} \): single TOF spectrum from \( W_{p} \) [2D] (s, V)
- \( W_{AV} \): averaged TOF spectrum [2D] (s, V)
- \( M \): covariance map [2D]
- \( M_{I} \): momentum image array [2D]
- \( Z \): zero array [1D or 2D]
- \( L \): fastframe length (number of points per spectrum)
- \( C \): fastframe count (number of spectra)
- \( N \): For loop N value
- \( F_{x} \): general force in x-direction (amu ms\(^{-2}\))
- \( F_{y} \): general force in x-direction (amu ms\(^{-2}\))
- \( F_{xx} \): component of force in x-direction for ion 1 (amu ms\(^{-2}\))
- \( \text{VL} \): velocity cluster (ms\(^{-1}\))
- \( \text{CL} \): co-ordinate cluster (m)
- \( \text{NORM} \): output of 'normalise?' dialogue
- \( \text{REV} \): output of 'reverse' control
- \( N_{\text{sim}} \): total number of simulations
**Scope Waveform Transfer.vi**

This VI transfers the waveform recorded on one of the DSO's input channels to the PC via the GPIB interface. The waveform can then be stored on the PC hard drive as a text file.

1. **Start**
2. **Error in**
3. **Select waveform for transfer**
4. **Collect information about waveform**
5. **Transfer waveform header**
6. **Format header**
7. **Transfer relevant amount of data**
8. **Save?**
   - **YES**
     - **Save to PC hard drive**
     - **Display data**
   - **NO**
8. **Format output to numerical**
9. **O/P waveform (W)**
10. **Error out**

**Load 1 Spectrum.vi**

This VI recalls a saved waveform, and displays it as a 2D (x-y) TOF spectrum.

1. **Start**
2. **Open Dialogue Window**
3. **Select file**
4. **Load file**
5. **Split into x and y arrays**
6. **Prepare x and y for display**
7. **Display spectrum**
8. **Finish**

**Load 2 Spectrum + scale.vi**

This VI recalls two saved waveforms, and displays them. The user can then scale the spectra arbitrarily while the 'enable' control is switched 'on'.

1. **Start**
2. **Open Dialogue Window 1**
3. **Select file 1**
4. **Load file 1**
5. **Open Dialogue Window 2**
6. **Select file 2**
7. **Load file 2**
8. **While loop**
   - **Split file 1: x, y**
   - **Split file 2: x, y**
   - **Display spectrum 1**
   - **Display spectrum 2**
   - **Scale file 2**
9. **While loop Enabled?**
   - **YES**
     - **Enabled?**
     - **Save?**
       - **YES**
         - **Open Dialogue Window**
       - **NO**
9. **NO**
10. **Display spectrum 1 and 2**
11. **Finish**

Note: The while loop allows adjustment of the scaling parameter while the VI is running.
Covariance Mapping vi front panel

- Error handling indicators
- Y-axis Average TOF spectrum
- Covariance map display
- Display control 'Enable' control (ON/OFF)
- Controls for Ranging filter
- X-axis Average TOF spectrum
- File path for map storage
Run Scope.vi

- **Start**
- **Error in**
- **Send 'RUN' ASCII command**
- **Wait 50 ms**
- **Finish**

This VI starts data collection on the DSO. Executing this VI is equivalent to pressing the Run/Stop button on the front of the DSO.

Data collection for C.M.vi

- **Start**
- **Error in**
- **Send Scope waveform**
- **Finish**

This VI automates the collection of one spectrum. Executing this VI is equivalent to pressing the 'Run' button on the front of the DSO, then waiting for data collection to stop, then transferring the waveform manually.

Ringing Filter.vi

- **Start**
- **Send waveform**
- **Finish**

This VI removes the instrumental 'ringing' effect from the TOF signal. This VI is used when collecting a covariance map.

State Test.vi

- **Start**
- **Error in**
- **Clear GPIB**
- **Send 'RUN?' ASCII query (see appendix 5)**
- **State?**

This VI repeatedly queries whether the DSO is collecting data or not. The VI waits until the DSO is no longer in "Run" mode, then finishes.

Peak Detect.vi

- **Initialise zero array, Z, N(y) long**
- **At each peak position, place y data into Z array until zero reached on -tive and +tive edge.**
- **Reconstruct 'filtered' spectrum, Wf**
- **Finish**

Note: The peak detect VI has two controls: 'threshold' and 'width'. The threshold is the minimum height a peak can have, and width is the minimum number of points in a peak.
FastFrame Info.vi

Start

Error in

Clear GPIB

Send 'HOR:FAST:LEN?; COUNT?'

Read 35 ASCII Characters across GPIB

Split into spectrum length (L) and number of spectra (C)

Finish

O/P L, C

Error out

This VI requests the DSO "fastframe" settings over the GPIB interface. The DSO returns the number of fastframes per spectrum, and the number of points per frame.

Calculation.vi

Start

Initialize 2D zero array (LxZ,) called Z

For loop, i=1 to C

put Z into shift register

Separate W_i into individual spectra (W) at (ixL)

Outer Product vi giving

Add to Shift Register

Z = Z + (W_i)

Divide contents of Shift Register by C

Finish

O/P <X>

Calculation.vi

Start

O/P L, C, W_i

For loop, i=1 to C

put Z into shift register

Index y values from F, define as y_k

Read y_k at (Lxj) + i

Outer Product vi giving

O/P For loop 2, Sum array, divide by C

O/P For loop 1, giving <X> (y values only)

Outer Product vi giving

Strip L x values, making x-axis for averaged spectrum

Build Average TOF spectrum from <X> (y) and E x values

O/P <X> (Average TOF spectrum)

Finish

O/P <X><Y>
Covariance Mapping.vi

Start

FastFrame select

Initialise zero array (LxL)

While loop. Put zero array on Shift Register

Data Collection for CMA

Ringing filter.vi

Calculation.vi

Calculation.vi

Subtract

Weight value from current iteration and add to Shift Register

YES

While loop Enabled?

NO

Display CM and Averaged TOF spectrum (Wsv)

Save CM and Averaged TOF spectrum (Wsv)

Finish

Load Covariance Map.vi

Start

Open Dialogue Window

Select file

Load file

Split into map (M) and spectrum (Wsv)

Split Wsv into x and y arrays

Display spectrum as x,y (horizontal) and y,x (vertical)

Display M

Finish
Covariance Map k.e. calculation vi front panel

Section display with projections on an energy scale

Operation controls

Covariance Map display

Projection scaling control

X-axis Average TOF display

Y-axis Average TOF display

Mid-point \( t_{0} \) controls

Ion mass and charge controls

Cursor positions in energy and momentum
Covariance Map k.e. calculation.vi section 1

Note: This VI can be used either to generate a projection of a section of the covariance map onto the x- and y-axes, or to convert the position of a cursor relative to the x and y direction mid-points into energy and momentum.

Start → Open Dialogue Window → Select file → Load file → Split into map (M) and spectrum (Wsv) (time) and WsdvW (signal) arrays

Generate empty clusters for cursor positions (c1 and c0)

Send y and Dcursor 1 on map

Read positions of cursor 2 and measure Δx and Δy

Convert Δx and Δy into momentum (p_x and p_y) and kinetic energy (E_x and E_y), using m_x, m_y, x0, y0, c, and ε.

Display p_x, p_y, E_x, and E_y

Covariance Map k.e. calculation.vi section 2 (C)

While loop: Put M, c1, and c0 into shift register

Read cursor positions on Map display → Read "mid-point x" and "mid-point y" and pass to x0 and y0

Generate k.e cross section → True?

From "Covariance Map k.e. Calculation.vi" section 2 (A)

To "Covariance Map k.e. Calculation.vi" section 2 (B)
Covariance Map k.e. calculation.vi section 2

The diagram below illustrates the definition of the variables used in the generation of the section of the map.

From 'Covariance Map k.e. Calculation.vi'
section 1 (A)

Read $n_x$, $n_y$ (± dimensions of section) from Front panel

Convert two-time arrays to energy ($S(t)$ and $E(t)$) and display, using $n_x$, $n_y$, $q_x$, $q_y$, and $E$

Display section

Index $S(t)$ for range of $x_{min}$ to $x_{max}$ and $y_{min}$ to $y_{max}$, generating section array

Sum indexed section of $M$ in $x$ and $y$ directions to generate projections.

Display projections

Scale $x$ and $y$ projections arbitrarily, generating $M_x$ and $M_y$

Update Shift Registers

To 'Covariance Map k.e. Calculation.vi'
section 1 (C)

While loop Enabled?

YES

Finish

NO
Synchronous Data Collection.vi

Start

Error in

Enter location of folder where data will be stored (path)

Measure start time \( t_{start} \)

While loop

Measure time at start of current iteration \( t_{current} \)

Display "true angle" and convert to string

Add to "start angle" and multiply by 2
This is 'True angle'

Build path for data from current iteration. \( PATH \)

NO

If has half wave plate rotated through 180°?

YES

Finish

Error out

Display spectrum

Save data to location in \( PATH \)

Split into \( x \) and \( y \) arrays

Run Scope.vi

State Test.vi

Synchronous Data Collection.vi

Scope waveform transfer.vi

Display spectrum
Control panel vi section 1

Note: this VI is used to control the data collection when using the DSO in conjunction with the Newport MM-4005 motion controller. When the VI is executed, 'Set RS-232 link vi' define the communication parameters (baud rate, port number, terminator). The VI then waits for an input from the operator. The VI can perform three different tasks: single translation or rotation or sequential data collection. Single movements are made using the 'Execute single movement' controls on the front panel, by entering the desired position and pressing either the 'press to rotate' or 'press to translate' controls. Sequential data collection is started using the 'Collection control' on the front panel. Spectra are collected by the DSO at the positions specified in the three numeric controls associated with either translation or rotation.
Control panel.vi section 2

From 'Control Panel.vi' section 1(A)

Sequence 2: 0

Dialogue box: 'Select motion'.
If rotate then set seq. local to T.

Case Structure 2

Case?

TRUE

Read start/stop positions, and display in message window.

FALSE

Read start/stop angles, and display in message window.

Case Structure 2

(T, F)

If Rote, then axis 1 is moved

If Translate, then axis 2 is moved

Sequence 2: 1

Case?

Sequence 2: 2

Note: The same stage is moved until the stop position is reached.

Sequence 3: 0

Select directory for input (PATH)

Verify communications using 'V E ' command (see appendix A6)

Sequence 3: 1

Send 'MG' command (A6) to turn on motors

Calculate increment size (STEP)

Wait 1000 ms

Sequence 3: 2

Send stage to 'start' position using 'PA' command (A6).

Sequence 3: 3

Sequence 3: 4

Sequence 3: 5

To 'Control Panel.vi' section 3(B)
Control panel vi section 3

Sequence Structure 4

While loop 2

Sequence 4: 0

Sequence 4: 1

Run Scope vi

Save Test vi

Scope waveform transfer vi

Format PATH from "current angle"

Save N to PATH.

Move stage by STEP using 'PR' command (see appendix A6)

Wait 1000 ms

Wait 'current position' greater than STOP?

Send 'MO' command (A6) to turn on motors

Send 'MO' command (A6) to turn on motors

Wait 1000 ms

Move axis 1 to desired position using 'PA' command (A6)

Move axis 0 to desired position using 'PA' command (A6)

To 'Control Panel. vi' section 1(B)

Note: Sequence 4:0 collects the TOF spectrum and saves it to the correct folder. Each spectrum is saved under a filename made either from the current angle or translator position.
Normalization and polar plotting vi front panel
Normalization and polar plotting.vi

Hierarchy diagram

Load directory and read angles.vi

TOF Matrix rotate.vi

Normalization and polar plotting.vi

Sort data with reverse option.vi

Energy and momentum calculations.vi

Calculate acc angle with p.sl.vi

Spectrometer acceptance.vi
This VI loads sequential spectra in the correct order. Given the sequential files (a) 9.5e-4, (b) le-3, (c) 1.05e-3 and (d) 1.1e-3, Windows lists the files in the order c, d, b, a. By loading all filenames and sorting them in ascending order, the correct sequence is recovered.

**Load directory and read angles vi**

1. **Start**
2. **UP PATH**
3. List directory
4. Remove digits from filename
5. "Size" array, giving number of angles, n,
6. Sort into ascending order
7. For loop 1
   - Convert each filename to three digit decimal
   - From D, remove y axis (ion signal) and build 2d array of all signal (S)
   - Build 1-D array of all angles in decimal (A)
8. Finish

**TOF Matrix rotate vi**

1. **Start**
2. **UP D, n**
3. Size dimension 1 of D array
4. For loop, N= n,
5. Rotate element 1 by n points
6. Rebuild D
7. Finish
8. OP D
Sort data with reverse option.vi

Energy calculation.vi

Spectrometer acceptance.vi

This VI reads the section of the data array according to the start and stop indices, which are defined by the start and stop cursor positions.

This VI can also reverse the section in the time dimension.

This VI converts the time array \( T_{\text{rec}} \) into an energy array \( E \).

Use dimensions of spectrometer to calculate \( E, E_1, E_2 \) electric field strengths.

Calculate initial velocity \( u \) using \( p \) and \( m \).

Calculate \( u \) and \( v \).

This VI calculates the position at which an ion of mass \( m \) and charge \( q \) with initial momentum \( p \) will strike the detector behind the channel plates.

Calculate \( x \) from \( t_{\text{acc}} \) and \( v \).

Finish

O/P \( D \)

Finish

O/P \( E \)

Start

Start

Start

\( \text{Input } q, m, \alpha, T_{\text{acc}}, t_{\text{acc}} \)

\( \text{Input } q, m, \alpha \)

\( \text{Input } \)
Calculate acc_angle with p in vi

For loop 1,
i = 1 to \{size of array\}

Index i\text{th element of } P, \text{ generating } P_i \text{ and negate giving } \pm P_i

Generate two 1-d arrays for \( \alpha_{\text{max}} \) as a function of \( P \) \( \alpha_{\text{max}} \) is maximum value of \( \alpha \).

While loops 1 (+P) and 2 (-P)

Use i from While loop to generate \( \alpha \)

Spline Interpolate.vi

Use \( \alpha \) from While loop to generate \( \pm P \)

For loop 2, N\text{-size of array, auto-index } \pm P

Generate same range of \( \alpha \) as in For loop 1

Spline Interpolate.vi

\( \text{Is spline of } \alpha_{\text{max}} \leq \alpha \)

\( \text{Calculate } c = \sin \alpha \) (correction factor value)

Build array of \( \pm C \) (correction factor) for \( \pm P \) on O/P of For loop 2

While loops 3 (+P) and 4 (-P)

Use i on each while loop to generate \( P \)

Index \( P \) at \( i \), giving \( P_i \)

Calculate \( P_{\alpha} = P_i / (\alpha / \text{const} \alpha) \)

Spline Interpolate.vi

\( \text{Is spline of } \alpha_{\text{max}} \leq \alpha \)

\( \text{Calculate } \pm C / D \text{ to generate } \pm D' \)

Case Structure 1 (T/F)

Pass \( D \) uncorrected to "normalised array"

Case Structure 2 (T/F)

\( \text{Calculate } \pm C / D \text{ to generate } \pm D' \)

Finish

\( O/P \ D \text{ or } D' \)
This VI is used to generate the TOF matrix. Two cursors are used to select a particular area of the matrix, corresponding to a particular ion. This data is then used to generate the IMI plot.

Sequence Structure 1
(0-3)

Sequence 1: 0

Dialog window

Select folder containing data (PATH)

Load directory and read angles.vi

If \( d \) is not in the range 0-360, then convert.

Index element 0,1,0 of \( D \) to generate time interval (\( \Delta t \))

Measure size of \( D \)

Index \( D \) row 0,1,0 to generate time array (\( T \))

Sequence 1: 1

'Add points' message with 'OK' button.

White loop 1

Rotation OK True?

YES

Press to finish TRUE?

YES

NO

TOF Matrix rotate.vi

NO

Collect 'number of points to shift' (\( n_D \))

\( D, n_D \)

To 'Normalisation and polar plotting .vi(2(A)
Normalisation and polar plotting vi section 2

Case structure 1
(T/F)

- Press to begin plotting true? YES
- NO

To 'Normalisation and polar plotting vi' 3(C)

Sequence Structure 2 (0-3)

Sequence: 0

- Read x, y from m and e from Front panel
- Start plotting routine to message window

Sequence: 1

- Read cursor y-positions, giving $t_{start}$ and $t_{stop}$
- Calc $I_x = \frac{\Delta t}{t_{stop} - t_{start}}$ (start and stop indices)
- $f_x, f_y$
- (time - $t_{start}$) / $D$
- Sort data with reverse option
- Extract 'offset' from $D$, and place in sequence local
- Subtract 'offset' from $D$, and place in sequence local
- Convert $E$ to momentum array $P$

Sequence: 2

- Index $F$ from $I_x$ to $I_y$, generating $\theta_{tec}$
- Define $\sum_{i=0}^n = f_{start}$
- Reverse $\theta_{tec}$ and define $\sum_{i=0}^n = f_{end}$

Sequence: 3

- Normalising to message window
- 2 Button dialogue box: ‘Normalise TOF data for detector geometry?’
- Select ‘Yes’ or ‘No’
- If ‘Yes’ then set ‘NORM’ to True.
- Case Structure (T,F) controlled by ‘NORM’
- Calculating p static with p in $\gamma$
- Note: The conversion of $E$ to $P$ is performed using the following equation:
  $P = \sqrt{2mE}$
Normalization and polar plotting vi section 3

From 'Normalization and polar plotting vi' 2(B)

Generate 2A(xmax) by N(xmax) empty array defined as MJ

Calculate number of p points per x div

For loop 1 (outer), N=2Nmax with 1 shift register

For loop 2 (inner), N=2Nmax with 1 shift register

Pass MJ through both shift registers

Pass D or D' into For loop 2

Pass A into For loop 2

Calc. x(3=x, 2)p and y(3=y, 2)p

Calculate the 'momentum index'

Pass MJ into intensity plot.

Update shift register with new MJ array

Display MJ in intensity plot.

Note: The section of the VI shown to the left places the relevant value from the section of the TOF matrix into the IM plot. This process is discussed in chapter 3.

From 'Normalization and polar plotting vi' 2(C)

Measure time separation of cursors on TOF matrix

Convert time separation into momentum using m, q and E

To 'Normalization and polar plotting vi' 2(A)

Threshold A for α

This is the 'angle index' α
dmax

Index M at (pmax, qmax), and put value into M at (α, A)
Front End.vi
front panel

Calculate momenta and angles.vi
front panel
Front End.vi hierarchy diagram

- Front end.vi
  - Align.vi
  - Asymmetric bond dist.vi
  -dl.vi
  - Mag2.vi
  - Sincos.vi
  - coords.vi
  - Calculate momenta and angles.vi
  - Acc1.vi Acc2.vi Acc3.vi
  - Reflect around zero.vi
  - vs1x.vi vs3y.vi

- 2 Plot results.vi
- 3 Plot results.vi
- Polar plot.vi
This VI uses Pythagoras' theorem to calculate the inter-nuclear separation of two ions \( a \) and \( b \), using the coordinates \((x_a, y_a)\) and \((x_b, y_b)\):

\[
 \text{rmag} = \sqrt{(x_a - x_b)^2 + (y_a - y_b)^2}
\]

This VI calculates the Coulomb force generated by each ion. The force is resolved in the x- and y-directions:

\[
 F_x = \frac{kq_a q_b}{r_{mag}^2} \cos \theta
\]

\[
 F_y = \frac{kq_a q_b}{r_{mag}^2} \sin \theta
\]

This VI calculates the amount of acceleration in the x- and y-directions, using Newton's second law, \( F = ma \):

\[
 \text{acc}_x, \text{acc}_y = \frac{F_x}{m}, \frac{F_y}{m}
\]

This VI calculates the change in velocity and position of each ion according to its acceleration:

\[
 \Delta v = \Delta v_0 + \Delta a \times \Delta t
\]

\[
 \Delta x = v_0 \times \Delta t + \frac{1}{2} a (\Delta t)^2
\]
This VI defines the time interval (dt) depending on the total elapsed time.

**Coords.vi**

1. Start
2. VP \(r_0, r_1\) and theta \((\theta)\)
3. Convert \(\theta\) to radians
4. Calculate \(\sin(\theta)\) and \(\cos(\theta)\)
5. Calculate \(y_1 = r_2 \cos(\theta)\)
6. Calculate \(x_1 = r_2 \sin(\theta)\)
7. Define \(x_1 = y_1 = 0\)
8. O/P \(x_1, x_2, x_3, y_1, y_2, y_3\) and \(\theta\)
9. Finish

**dt.vi**

1. Start
2. VP \(r\)
3. If \(r\) in range 0 - 0.17
   - YES: Set dt to 0.02
   - NO: Is \(r\) in range 0.1 - 17
   - YES: Set dt to 0.04
   - NO: Is \(r\) in range 1 - 5
     - YES: Set dt to 0.04
     - NO: Is \(r\) in range 5 - 100
       - YES: Set dt to 0.5
       - NO: Set dt to 1
4. Finish

This VI converts the bend-angle and bond-length to Cartesian co-ordinates.
**Align.vi**

Start

Read $\theta_{\text{max}}$ from front panel

Define $a = -1/(2\Phi_{\text{max}})$

Calculate $y = a\Phi_{\text{max}}^2 + \Phi_{\text{max}}$

Calculate $x = 1 + (-4y)^{1/2}$

Generate random number $n_{\text{rand}}$

Calculate $y_{\text{cub}} = n_{\text{rand}} < y$

Calculate $x_{\text{mid}} = 1 - (2y_{\text{cub}})^{1/2}$

Generate random number $n_{\text{rand}}$

If $n_{\text{rand}} > 0.5$

Negate $x$

NO

Finish

O/P alignment angle, $\theta$

This VI generates the angle of alignment between the molecule and the laser polarization direction using a Monte Carlo technique.

---

**Asymmetric bend dist.vi**

(Asymmetric bend dist.vi is identical, but the O/P is $r$)

Start

UP mid, $\theta_{\text{cub}}$, $W_1$, $W_2$ and $H$

Define $a_1 = (W_1 - \text{mid})/2$

Define $a_2 = (W_2 - \text{mid})/2$

Calculate $y_i = a_i(W_i)^2 + W_i$

Case Structure 1 (T/F)

Calculate $y_{\text{cub}} = n_{\text{rand}} < y$

Calculate $x_{r} = (a_1^2W_2 + a_2^2W_1)/2$

Calculate $\theta = \text{mid} + x_{r}$

Finish

O/P bend angle, $\theta$

This VI generates the molecular bend angle using a Monte Carlo technique.
Calculate momenta and angles

Start

Bundle $x_i$, $y_i$, and $z_i$ into co-ord cluster $CL$

Generate an empty six elements velocity cluster, $VL$

Define time $t=0$

While loop, put $CL$, $VL$, and $t$ into shift register.

Calculate momenta and angles

Unbundle $CL$

Bundle $x_i, y_i, z_i$ into co-ord cluster $CL$

Calculate $CL + ACL$ and pass to shift register as $CL$

Calculate $\omega_i = \tan^{-1}(v_{ix}, v_{iy})$

Convert $\omega_i$ from degrees to radians

Calculate $E_i = \frac{1}{2} m_i (v_{ix}^2 + v_{iy}^2 + v_{iz}^2)$

Calculate $p_i = \sqrt{2m_i E_i}$

Finish

Stop

O/P $\omega_i, \omega_j, \omega_k, F_i, F_j, F_k$

O/P $\omega_i, \omega_j, \omega_k, F_i, F_j, F_k$

O/P $\omega_i, \omega_j, \omega_k, F_i, F_j, F_k$
Reflect around zero vi

Start

UP \( \alpha_1, \alpha_2, \alpha_3 \)

\[ \alpha_{1,2} < 0? \]

TRUE

Negate \( \alpha_{1,2} \)

FALSE

\[ \alpha_{1,2} > 90? \]

TRUE

Calculate \( \alpha_{1,2} - 2(\alpha_{1,2} - 90) \)

FALSE

Finish

This VI ensures that each ion is travelling within one quadrant, and that the same orientation with respect to the laser polarisation is maintained.
Note: In '2 plot results.vi', ions 1 and 3 are identical, hence the results from these simulations are combined. For example, in the (2,2,2) channel in carbon dioxide, the results from the two oxygen ion is combined.
In '3 plot results.vi', ions 1, 2, and 3 are treated individually. Start.

Using For loop, auto-indexed by dim 1 of and Pass am 2 » tmpl to shift registers. Index elements 0,1,2 generating p, p2, p3 fixing A, calculating CO2 (Bj, (0, thresholding P for P i, P j, generating indices n^, thresholding A, generating indices nA, Add 1 to element (p i, A j) of tmpl, Add 1 to element (p i, A j) of tmpl. Pass updated arrays tmpl and tmpl to shift register tmpl. When For loop finished, display tmpl and tmpl in intensity plots.

Case structure: Save control W E S TRUE? Build arrays of (P and D 1), (P and D 2), and (P and D 3) and save to spreadsheet.
Polar plot vi

Note: The data in $D_{work}$ depends on the selection made in 'Front End vi', using the '1 ion select' and '3 ion select' controls.

Note: $4\beta_{min}$ is used as the simulation program only simulates one quadrant (0° to 90°) as the behaviour of the ions is symmetrical about the laser polarisation and about an axis perpendicular to the polarisation.

Note: $l_{p}$ is the length of the p dimension, and $l_{b}$ is the length of the $b$ dimension.

Start

For loop 1

For $i = 1$ to $l_{b}$

Index $D_{work}$ at $(i, j)$

For loop 2 (outer), $j = 1$ to $l_{p}$

For loop 3 (inner), $j = 1$ to $l_{p}$

Generate $2\beta_{select}$ by $N_{shift}$ empty array defined as $M_{p}$

Calculate number of $p$ points per $x$ div

Attribute node for $M_{p}$ display defined $s_{x} = \beta_{select} / 2 \beta_{p}$ and $\Delta s_{x} = \beta_{select} / N_{shift}$

Measure dimensions of $D_{work}$ as $l_{p}$ and $l_{b}$

Pass $M_{p}$ through both shift registers

Pass $D_{work}$ into For loop 3

Index at $D_{work}$

For loop 3

Output $D_{work}$ from For loop 1

Build array of $(D_{x} - D_{y}) / 2$ defined as $D_{work}$

Calculate the momentum index $P_{x} \cos(\theta) / \cos(\beta) - 2 \beta$

Calculate momentum index $P_{y} \cos(\theta) / \cos(\beta) - 2 \beta$

Pass $M_{p}$ into For loop 3

Threshold $A$ for $P_{x}$

Threshold $A$ for $P_{y}$

Display $M_{p}$ in Intensity plot.

Update shift registers with new $M_{p}$ array

Finish

The process of generating $D_{work}$ is illustrated below.
Start

Read \( N_{\text{seq}} \) (total number of simulations)

Build two 3x\( N_{\text{seq}} \) empty arrays \( P_{\text{seq}} \), and \( A_{\text{seq}} \)

While loop with two shift registers, where \( i \) is the current iteration number

Pass \( P_{\text{seq}} \) and \( A_{\text{seq}} \) to shift registers

Note: The two intermolecular bonds are the same length, hence \( r_{1} = r_{2} = r \)

Asymmetric fracture and angles vi

Calculate

- \( P_{1} \), \( P_{2} \), \( P_{3} \)
- \( \alpha_{1}, \alpha_{2}, \alpha_{3} \)
- \( \beta_{1}, \beta_{2}, \beta_{3} \)
- \( \gamma_{1}, \gamma_{2}, \gamma_{3} \)

Replace elements \((0,0,0), (1,0), \) and \((2,0)\) of \( P_{\text{seq}} \) with \( P_{1}, P_{2}, P_{3} \) respectively

Redefine \( \alpha_{1} = \alpha_{2} = 90 \), \( \alpha_{3} = 90 - \alpha_{1} \), \( \alpha_{4} = 90 - \alpha_{2} \)

Asymmetric bend distance vi

Calculate

- \( \alpha_{1}, \alpha_{2}, \alpha_{3} \)
- \( \alpha_{4}, \alpha_{5}, \alpha_{6} \)

Replace elements \((0,0,0), (1,0), \) and \((2,0)\) of \( A_{\text{seq}} \) with \( \alpha_{1}, \alpha_{2}, \alpha_{3} \) respectively

Reflect around zero vi

Press to display control

Case structure 1

2 ion

Case Structure 2

(T/F)

Case Structure 3

(T/F)

Case Structure 4

(T/F)

Display mode

2 ion select

Case T

Case F

3 ion

3 ion select

Ion 1

Ion 2

Ion 3

Polar plot vi

Polar plot vi

Polar plot vi

Polar plot vi
Least-squares for equal momentum step vi

front panel

- IMI data display (Cartesian)
- Combined and scaled Monte Carlo data display (Cartesian)
- Least-squares between IMI and Monte Carlo data
- Number of channels control
- "Enable" control (on/off)
- Simulation channel scaling factors control
- All channel scaling control
- Sum of all least squares values

Least-squares for equal momentum steps vi hierarchy diagram

- Load experimental IMI data for hi
- Scale n quad for arbitrary scale for equal mom steps vi
Load experimental IMI data for Isf.vi

Start
- Open Dialogue Window
  - 'Select IMI data file'
- Select file
- Load selected file, defined as D
- Measure dimensions of D array, dim_x and dim_y
- Remove the 'header' from the data.
- For loop 1
  - i=1 to dim_y
  - Input D' and rotate clockwise, and reflect horizontally, giving D''
- Redefine D' as D
- Reverse each y array defined D'
- Measure dimensions of D' array, dim_x and dim_y
- Remove first row of D'(ch) in x direction
- Define D'' as D'(ch) 'scaling factors'
- Measure dimensions of D''(ch), dim_x, dim_y and dim_z
- Create zero array Z using dim_x and dim_y
- For loop 1
  - i=1 to dim_x
  - j=1 to dim_y (auto-index Z) (ch)
  - 'scaling factors' at input
  - Multiply each x element by relevant scaling factor
  - Add each scaled element to Z
- Remove first row of Z in x direction
- Define Z=D''(sc) as 'combined and scaled quadrant of simulated signal'
- Remove first row in a direction
- For loop 2
  - i=1 to dim_y of D''(sc)
  - Reflect D''(sc) around x axis, generating D'(sc)
  - Build array of D=(D'D''(sc))
  - Remove last column (y direction) from Z and replace with zeros
- Define D=D''(sc)
- Finish

Note: D''(ch) is made from the same ion (e.g. D''(ch)) but over n_i channels.

This VI loads an IMI file as generated by 'Normalisation and polar plotting.vi' and ensures that it is in the same format as the Monte Carlo simulation results.

Scale n quads with arbitrary scale for equal mom steps.vi

Start
- Define D=D''(sc)
- For loop 2
  - i=1 to dim_x
  - Reflect D''(sc) around x axis, generating D''(sc)
  - Build array of D=(D'D''(sc))
  - Remove last column (x direction) from Z and replace with zeros
- Define D=D''(sc)
- Finish

This VI loads a number of Monte Carlo simulation files, scales each independently the generates an array of the sum of all of the channels.
Least-squares for equal momentum step vi

Start

Read 'number of channels', n

For loop i=1 to n

Dialogue box 'Select file for channel (i+1)'

Load selected file, and define as D_{im}^{(q)}

On O/P of For loop, build array of D_{im}^{(q)} to D_{im}^{(m)}, defined as D_{im}^{(m)}

Display D in intensity plot

Read 'scaling factors'

Scale n quads with aibtratios a_s

On O/P of For loop, build array of D_{im}^{(m)} to D_{im}^{(sc)} defined as D_{im}^{(sc)}

Display D - D_{im}^{(sc)} in intensity plot

Calculate D = D_{im}^{(sc)} and sum over all array elements, giving least-squares value

Display least-squares value

'Run lst' control?

TRUE

FALSE

Finish

Note: Dialogue box displays 'Select file for channel 3' for i=2

Load experimental RAM data for channel (i+1)

Read 'number of channels', n

For loop i=1 to n

Dialogue box 'Select file for channel (i+1)'

Load selected file, and define as D_{im}^{(q)}

On O/P of For loop, build array of D_{im}^{(q)} to D_{im}^{(m)}, defined as D_{im}^{(m)}

Display D in intensity plot

Read 'scaling factors'

Scale n quads with aibtratios a_s

On O/P of For loop, build array of D_{im}^{(m)} to D_{im}^{(sc)} defined as D_{im}^{(sc)}

Display D - D_{im}^{(sc)} in intensity plot

Calculate D = D_{im}^{(sc)} and sum over all array elements, giving least-squares value

Display least-squares value

'Run lst' control?

TRUE

FALSE

Finish
Appendix 5. Tektronix TDS-744A and Newport MM4005 ASCII commands

Below is a list of the ASCII commands used in the present work. These lists are not exhaustive, but are intended as a guide to the commands used within the VIs presented in appendix 5. When the commands are a mix of lower- and upper case, the instruments will perform the same operation when only the upper-case command is send.

A5.1 Tektronix TDS-744A commands

Below is a list of the ASCII commands used in the present work, followed by a brief description, and a reference to the VI in which the command is used.

<table>
<thead>
<tr>
<th>Command</th>
<th>Description</th>
<th>Used in VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACQuire:STATE RUN</td>
<td>Starts acquisition</td>
<td>1</td>
</tr>
<tr>
<td>ACQuire:STATE?</td>
<td>Returns 0 or 1 depending on whether DSO is acquiring (1) or not (0)</td>
<td>2</td>
</tr>
<tr>
<td>CH&lt;x&gt; ON</td>
<td>Turns on channel x</td>
<td>3</td>
</tr>
<tr>
<td>CURVe?</td>
<td>Transfers waveform from channel specified in DAT:SOU &lt;wfm&gt; to the PC in format specified in DAT:ENG</td>
<td>3</td>
</tr>
<tr>
<td>DATa:ENCdg RPB</td>
<td>Sets waveform format. RPB refers to R P Binary encoding (positive integer data point representation with the most significant byte first)</td>
<td>3</td>
</tr>
<tr>
<td>DATa:SOUrc &lt;wfm&gt;</td>
<td>Sets the waveform (&lt;wfm&gt;) to be transferred by the CURVe? command</td>
<td>3</td>
</tr>
<tr>
<td>DATa:WIDth 2</td>
<td>Sets the number of bytes per data point transferred using the CURV? command</td>
<td>3</td>
</tr>
<tr>
<td>HORIZontal:FASTframe: LENGth?</td>
<td>Queries the length of each fastframe frame</td>
<td>4</td>
</tr>
<tr>
<td>HOR:FAST:COUNt?</td>
<td>Queries the number of fastframe frames</td>
<td>4</td>
</tr>
<tr>
<td>IDN?</td>
<td>Returns the DSO identification code</td>
<td>Test</td>
</tr>
<tr>
<td>SELECT:CH&lt;x&gt; ON</td>
<td>Displays channel x</td>
<td>3</td>
</tr>
<tr>
<td>WFMPre:&lt;wfm&gt;: NR_Pt?</td>
<td>Queries the number of points in the waveform specified in DATa:SOURce &lt;wfm&gt;</td>
<td>3</td>
</tr>
<tr>
<td>WFMPre:&lt;wfm&gt;: PT_Off?</td>
<td>Queries the trigger point within the waveform specified in DATa:SOURce &lt;wfm&gt;</td>
<td>3</td>
</tr>
<tr>
<td>WFMPre:&lt;wfm&gt;: XINcr?</td>
<td>Queries the horizontal sampling interval of the waveform specified in DATa:SOURce &lt;wfm&gt;</td>
<td>3</td>
</tr>
<tr>
<td>WFMPre:&lt;wfm&gt;: YMUlt?</td>
<td>Queries the vertical scale factor of the waveform specified in DATa:SOURce &lt;wfm&gt;</td>
<td>3</td>
</tr>
</tbody>
</table>
WFMPre:<wfm>: YO? Queries the vertical position of the waveform specified in DATa:SOURce <wfm> 3

WFMPre:<wfm>: YZEro? Queries the vertical offset voltage of the waveform specified in DATa:SOURce <wfm> 3

The 'Used in VI' column is identified as follows:
1. Run Scope.vi
2. State Test.vi
3. Scope Waveform Transfer.vi
4. FastFrame Info.vi

Test is a simple GPIB program used to send ASCII commands manually.

A5.2 Newport MM4005 Commands

Below is a list of the ASCII commands used in the present work.

<table>
<thead>
<tr>
<th>Command</th>
<th>Description</th>
<th>Used in VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>VE</td>
<td>Verify. Used to verify communications with MM4005 by requesting controller version number</td>
<td>C</td>
</tr>
<tr>
<td>MO</td>
<td>Motor On. Used to switch Motor(s)</td>
<td>C</td>
</tr>
<tr>
<td>[xx] PA [nn]</td>
<td>Parameter Absolute. Moves axis number [xx] to [nn] units (degrees/mm) from zero</td>
<td>C</td>
</tr>
<tr>
<td>[xx] PR [nn]</td>
<td>Parameter Relative. Move axis number [xx] through [nn] units (degrees/mm) relative to position when command sent</td>
<td>C</td>
</tr>
</tbody>
</table>

Where C is Control Panel.vi.
Appendix 6. List of conference proceedings

XXII$^{nd}$ International Conference on Photonic, Electronic and Atomic Collisions, Santa Fe, USA (July 2001)
*High intensity femtosecond laser interactions with HD$^+$ and H$_2^+$*
*Ion momentum imaging of carbonyl sulphide geometry in high intensity femtosecond laser pulses*
*Spatially resolved ionization processes in high intensity femtosecond laser pulses*

10th International conference on the Physics of Highly Charged Ions, Berkley, California (July 2000)
*A detailed study of multiply charged ion production within a high intensity laser focus*

*H$_2^+$ ion beams in intense laser fields*

Institute of Physics Congress, Brighton, UK (March, 2000)
*H$_2^+$ ion beams in intense laser fields*
XXI* International Conference on the Physics of Electronic and Atomic Collisions, Sendai, Japan (July 1999)


Beams of molecular ions in intense laser fields


Momentum imaging of ground state and vibrationally excited $H_2O$ using a femtosecond laser pulse of intensity $10^{17} Wcm^{-2}$


Triatomic molecular structure studied by ion-momentum imaging and Monte Carlo simulation

Ultra intense laser interactions and applications, Elounda, Crete, Greece, (May 1999)


Momentum imaging of carbon dioxide using 55fs pulses

25th National Conference on Atomic, Molecular and Optical Physics, University of Manchester, UK, (April 1999)


Triatomic molecular structure studied by ion-momentum imaging and Monte Carlo simulation

Conference on the Application of Accelerators in Research and Industry, Denton, USA (Nov 1998)


Ion beams as targets for high intensity femtosecond laser studies

IX* International Conference of the Physics of Highly Charged Ions, Bensheim, Germany (September 1998)

Short pulse laser interactions with positive ions

6th European Conference on Atomic and Molecular Physics, Sienna, Italy (July 1998)


Alignment and bending of CO$_2$ by intense femtosecond laser pulses

20th international conference on the Physics of Electronic and Atomic collisions.
Vienna, Austria (July 1997)


High intensity laser fragmentation of vibrationally excited CO$_2$
Appendix 7. Publications

Preface
Chapters 2 to 5 of this thesis have only covered two of the papers published as part of my Ph.D. For completeness, the following appendix contains all of my publications to date, as listed below.

A7.1 Multielectron-dissociative-ionization of SF₆ by intense femtosecond laser pulses

A7.2 High-intensity femtosecond laser interactions with vibrationally excited CO₂

A7.3 Alignment and bending of CO₂ by intense femtosecond laser pulses

A7.4 Geometry modification and alignment of H₂O in an intense femtosecond laser pulse

A7.5 Sub-pulselength resolution of bond softening and Coulomb explosion using polarization control of laser-induced alignment
Posthumus J H, Plumridge J, Taday P F, Sanderson J H, Langely A J, Codling K and Bryan W A

A7.6 Short pulse laser interactions with positive ions
Physica Scripta T80 534 (1999)

A7.7 Laser-induced Coulomb explosion, geometry modification and reorientation of carbon dioxide

A7.8 Fast beam study of a H$_2^+$ ions in an intense femtosecond laser field

A7.9 A detailed study of multiply charged ion production within a high intensity laser focus
Physica Scripta T92 119 (2001)
Appendix 7.1

Multielectron-dissociative-ionization of SF$_6$ by intense femtosecond laser pulses

J H Sanderson§, R V Thomas†, W A Bryan†, W R Newell†, P F Taday‡ and A J Langley‡

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Received 22 May 1997, in final form 24 July 1997

Abstract. The first detailed observations of the multielectron-dissociative-ionization of sulphur hexafluoride have been made using 60 fs laser pulses at 750 nm and $7 \times 10^{15}$ W cm$^{-2}$. The fragmentation pattern displays features similar to those found in experiments with diatomic and triatomic molecules, such as a tendency towards symmetrically dissociative channels and fragment kinetic energies which for all channels are consistent with a Coulomb explosion at a single, critical, internuclear separation.

1. Introduction

During the last ten years the dynamical behaviour of simple molecules (largely diatomic but also some triatomic and planar polyatomic) in laser pulses has been studied, notably by the Reading group, at increasing intensity and progressively shorter laser pulses, see for example Codling and Frasinski (1993). Many of the important features of molecular dynamics in femtosecond laser pulses are now beginning to be understood, such as the phenomenon of multielectron-dissociative-ionization (MEDI), in which many electrons (up to 20) are rapidly removed from a molecule which subsequently Coulomb explodes producing atomic ions of high kinetic energy. Such Coulomb explosions can only be induced otherwise by highly charged ion impact (Mathur et al 1992), or in collisions between high-energy molecular ions and a foil target (Vager et al 1989). Electron impact or single-photon absorption, cannot produce the high stages of ionization which cause MEDI, although the removal of two electrons leading to double dissociative ionization (DDI) is common (Hitchock et al 1978). The DDI process involves the release of much lower energy, and cannot cause a polyatomic molecule to disintegrate into atomic ions. In the case of MEDI induced by femtosecond laser pulses, the process has been found to be very symmetrical and to give rise to kinetic energies of roughly half the expected Coulomb explosion energy, this is understood to result from stretching of the molecular bonds prior to multiple ionization (Posthumus et al 1996). More recently, large complex molecules and clusters have also been subjected to femtosecond laser pulses (Ledingham et al 1995, Shao et al 1996) either as a diagnostic tool or a way of generating short-wavelength light. In this work we have studied the fragmentation dynamics of the three-dimensional molecule SF$_6$, when subjected to ultrashort (60 fs) laser pulses of 750 nm wavelength and intensity up to $7 \times 10^{15}$ W cm$^{-2}$.

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0953-4075/97/204499+09$19.50 © 1997 IOP Publishing Ltd
2. Experimental

The apparatus used for this experiment is a Wiley-McLaren-type time-of-flight (TOF) mass spectrometer (Wiley and McLaren 1955). The spectrometer has a total flight path of 12.53 cm with a pair of microchannel plates of diameter 25 mm used to detect the ions. The apparatus is housed in a 200 mm diameter vacuum tank pumped by a turbo-molecular pump giving an ultimate background pressure of about $4 \times 10^{-10}$ Torr. The test gas is introduced into the interaction region by a hypodermic needle, the tip of which is situated 10 mm from the laser focus.

The ion signal is fed through a pre-amplifier into an EG&G turbo multichannel scalar (MCS). The MCS has a channel width of 5 ns with zero dead time between channels and can also count more than one event per channel.

The laser system (Langley et al 1994) consists of a Tsunami oscillator, pumped by an argon ion laser, which produces 55 fs pulses with an 82 MHz repetition rate at a centre wavelength of 750 nm. The pulses are stretched, by a pair of BK7 prisms in a double pass configuration, to approximately 750 fs. The stretched pulses are then amplified in a three-stage dye amplifier, using laser dye LDS 751, pumped by a frequency-doubled Nd:YAG laser with a repetition rate of 10 Hz. The amplified pulses are compressed back to around 55 fs with a 40 mm block of SF10 glass. The energy in the compressed pulse is 60 $\mu$J. The pulses stretch to 60 fs on passing through the experiment input window. A 22 mm focal length on-axis parabolic mirror is situated in the interaction region and focuses the laser beam to a near-diffraction limited spot of 4.2 $\mu$m.

To ensure that there is no more than a $\pm5\%$ fluctuation in the energy of the laser pulses entering the experiment, the start pulse to the MCS is gated by monitoring the reflection from the input window with a photodiode. The photodiode pulse height has previously been calibrated against the laser pulse energy and found to be linearly proportional to it. The photodiode pulses are amplified and passed through a single-channel analyser which has a window set to 10% of the desired pulse height. The pulses which are within the chosen range are used to provide the start pulse for the MCS. The laser pulse shape is also monitored with an autocorrelator so that any drift in pulse width can be detected; the pulse-to-pulse variation in width is less than $\pm5$ fs.

Taking into account the pulse energy of 50 $\mu$J and the size of the focus, which is 4.2 $\mu$m, a calculation of the peak intensity can be made which yields a figure of $7 \times 10^{15}$ W cm$^{-2}$.

In order to determine which ions are present when SF$_6$ is dissociated and ionized by the femtosecond laser pulses and which fragmentation channels are involved, we have varied the extraction field from 20 V cm$^{-1}$ to 300 V cm$^{-1}$, recorded spectra with both vertical and horizontal polarizations and varied the laser pulse intensity from $7 \times 10^{15}$ W cm$^{-2}$ to $4.3 \times 10^{14}$ W cm$^{-2}$.

3. Results

Figure 1 shows the fragment ion TOF spectrum for SF$_6$ recorded with an extraction field of 300 V cm$^{-1}$. The first feature of note is that no SF$_5^+$ ions are observed, the most massive fragment ion being SF$_4^+$. This is the only feature of the ion mass spectrum which has previously been commented upon in relation to short-pulse laser-induced dissociative ionization. The observation was made by Lynga et al (1996) in their work which concerned high-harmonic generation. This observation is in fact to be expected as the parent ion is known to dissociate, over a period of around 1 ps, into a range of fragment ions (Creasey et al 1991, 1993). That part of the fragmentation pattern which extends from S$^+$ to SF$_5^+$,
in figure 1, is typical of the distribution of ions formed by both electron impact ionization and synchrotron photo-ionization (Hitchcock and Van der Weil 1979, Hitchcock et al 1978) and is the signature of $SF_6^{+}$ production. In general, the parent ion is usually prominent in experiments using femtosecond pulses (Ledingham et al 1995). Although it has been shown that femtosecond pulses can overcome the propensity of certain molecules to predissociate during multiphoton ionization, this is impossible in the case of $SF_6$ as the dissociation occurs post ionization.

The appearance of doubly charged fragments, $SF_6^{2+}$ and $SF_6^{2+}$, indicates that the parent ion has been doubly charged. The formation of $SF_6^{2+}$ also leads to DDI in which $SF_6^{2+}$ dissociates into two fragment ions typically $SF_n^{+}$ and $F^{+}$ ($0 \leq n \leq 5$) (Hitchcock et al 1978). Although some of the $F^{+}$ ions observed result from DDI, the majority result from MEDI associated with high-intensity short-pulse laser radiation (Codling and Frasinski 1993). In trying to understand the MEDI process in $SF_6$ we need only be concerned with the interaction between the laser pulse and multiply ionized $SF_6$ molecule, there is no interaction between the laser pulse and any of the fragment ions, $S^{+}$ to $SF_n^{+}$, because the pulse length of 60 fs is short with respect to the dissociation timescale of $SF_6^{2+}$. In addition to $F^{+}$, the $S^{2+}$, $S^{3+}$, $S^{4+}$ and $S^{5+}$ fragments are also associated with the MEDI process. The existence of $F^{2+}$ ions is indicated by the distortion to the $S^{3+}$ and $S^{4+}$ peaks, see figure 1. The unresolved status of the $F^{2+}$ ions is due to their high kinetic energy, leading to the creation of a forward peak and backward peak which have nearly the same positions as the $S^{3+}$ and $S^{4+}$ peaks respectively. Normally this overlap could be confirmed simply by rotating the polarization of the laser light by 90° (Normand et al 1992a, b) since it is known that the energetic fragments produced in the MEDI process are strongly aligned with the laser field. Therefore when the field is parallel to the TOF axis a double peak structure is observed but when the field is perpendicular to the TOF axis either a single peak is observed (Hatherly et al 1990), because there is no intrinsic momentum along the spectrometer axis, or no peak is observed, as the ions escape the acceptance angle of the detector, due to their momentum perpendicular to the spectrometer axis. However, figure 1 shows that there is little difference between the TOF spectra obtained with the polarization perpendicular and parallel. This is undoubtedly due to the highly spherically symmetric nature of the $SF_6$ molecule, which we will return to later. In order to resolve the overlap in the peaks, another technique must be used, which is simply to vary the extraction field gradually, and compare the resulting TOF spectra (Normand et al 1992a). As the extraction field is reduced the separation of the
energetic peaks becomes greater, as does the separation of the individual mass peaks, but crucially the two processes take place at a different rate so that energetic fragment peaks appear to move through the non-energetic mass peaks.

In figure 2, recorded with an extraction field of 75 V cm\(^{-1}\), the forward and backward energetic F\(^{2+}\) ions become distinct from the S\(^{3+}\) and S\(^{4+}\) ions, in addition, the intensity of the energetic fluorine ions relative to the very low kinetic-energy fragment ions, S\(^{2+}\) to SF\(_2\), has decreased considerably, due to a reduction in the angular acceptance of the detector with decreasing extraction field. The very low kinetic-energy ions from S\(^{2+}\) to SF\(_2\) show the same peak sizes relative to each other, for both extraction fields. We can then deduce that the relative abundances of S\(^{3+}\) and S\(^{4+}\) to S\(^{2+}\) are also the same as in the 300 V cm\(^{-1}\) extraction case, as they are also produced with very low kinetic energy. Therefore, in figure 1 the F\(^{2+}\) doublet is dominant over the S\(^{3+}\) and S\(^{4+}\) signal.

The spectra recorded as a function of laser intensity are given in figure 3. In this case the extraction field was 300 V cm\(^{-1}\) with the S\(^{3+}\) and S\(^{4+}\) ion peaks not resolved from the F\(^{2+}\) ion. As the intensity is reduced from 7 \times 10\(^{15}\) W cm\(^{-2}\) in figure 3(a) to 4 \times 10\(^{15}\) W cm\(^{-2}\) in figure 3(b) the count rate decreases overall, with no significant change in the pattern of the spectrum. However, at 1.8 \times 10\(^{15}\) W cm\(^{-2}\) in figure 3(c) the highest stages of ionization S\(^{5+}\) and F\(^{3+}\) disappear and at 8 \times 10\(^{14}\) W cm\(^{-2}\) in figure 3(d) the F\(^{2+}\), S\(^{3+}\) and S\(^{4+}\) ions have begun to decrease relative to the F\(^{+}\) signal. Finally, at 4.3 \times 10\(^{14}\) W cm\(^{-2}\) in figure 3(e) the only fragment ions remaining are SF\(_2\) and F\(^{+}\). The F\(^{+}\) ions present in figure 3(e) are associated with the dissociation of SF\(_6\) and as such have a visibly narrower TOF spread associated with a lower kinetic energy.

Table 1 gives the measured peak energies of each of the MEDI fragments. All of the sulphur peaks are centred about 0 eV indicating that symmetric channels of MEDI are predominant; the symmetry of the MEDI processes in diatomic and triatomic molecules has been discussed by Frasinski \textit{et al} (1994) and Codling \textit{et al} (1991). In the case of SF\(_6\), symmetrical channels imply that the two fluorine atoms on each axis have the same stage of ionization, treating each axis as a triatomic molecule sharing the same sulphur atom gives allowed channels; F\(^{M+}\)-S\(^{N+}\)-F\(^{M+}\), F\(^{L+}\)-S\(^{N+}\)-F\(^{L+}\) and F\(^{P+}\)-S\(^{N+}\)-F\(^{P+}\). The superscripts L, M, N and P indicating the degree of ionization are not necessarily the same in order to leave S\(^{N+}\) with zero kinetic energy. In the simplest scenario, all of the fluorine ions will be of the same charge state, so that M = L = P. The peak kinetic energies of the fluorine fragments are also given in table 1 with the full kinetic-energy distributions given in figure 4. The F\(^{+}\) ions result from both DDI (Hitchcock \textit{et al} 1978) and MEDI and two...
distributions are clearly evident in the F⁺ energy distribution with a low-energy peak around 2 eV and a high-energy shoulder appearing around 17 eV, which tails off to 50 eV. Although the DDI process is an adequate explanation for the 2 eV ions, it is possible that some of the low-energy F⁺ ions result from bond softening (Zavriyev et al 1990). The shoulder at 17 eV represents the peak of the distribution due to MEDI. The F²⁺ distribution is wide with a FWHM of 25 eV and a maximum at around 50 eV; the F³⁺ energy distribution is wider with a FWHM of 60 eV and a maximum at around 90 eV. These high kinetic energies result from the MEDI process which, as we have already seen from the mean zero kinetic energies of the sulphur peaks, favours symmetrical channels of dissociation for SF₆.

Table 1. Observed Coulomb explosion fragment ions of SF₆.

<table>
<thead>
<tr>
<th>Fragment</th>
<th>Peak energy (eV)</th>
<th>FWHM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S⁺</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>S²⁺</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td>S³⁺</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>S⁴⁺</td>
<td>0</td>
<td>1.2</td>
</tr>
<tr>
<td>S⁵⁺</td>
<td>0</td>
<td>3.0</td>
</tr>
<tr>
<td>F⁺</td>
<td>2, 17</td>
<td>—</td>
</tr>
<tr>
<td>F²⁺</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>F³⁺</td>
<td>90</td>
<td>60</td>
</tr>
</tbody>
</table>

Figure 3. TOF spectra for SF₆ recorded with an extraction field of 300 V cm⁻¹ and intensities of (a) 7 × 10¹⁵ W cm⁻², (b) 4 × 10¹⁵ W cm⁻², (c) 1.8 × 10¹⁵ W cm⁻², (d) 8 × 10¹⁴ W cm⁻², (e) 4.3 × 10¹⁴ W cm⁻², see figure 1 for designation of peaks.
4. Discussion

It is known that the kinetic energies resulting from MEDI exhibit a strong relationship with the energies which would be expected from Coulomb explosion (Posthumus et al 1995). Typically the kinetic energies observed are consistent with Coulomb explosions occurring at a single critical internuclear separation for all channels, \( R_c = \frac{1}{C_m} R_e \), where \( C_m \) is a constant and \( R_e \) is the equilibrium internuclear separation. The constant \( C_m \) has been found to be 0.45 for molecules consisting of light atoms such as C, O, and N. The existence of a single critical internuclear separation \( R_c \) for diatomic molecules has been elegantly explained by Posthumus et al (1996) using an over-the-barrier approach.

Using the known properties of MEDI, the fragmentation symmetry and critical internuclear separation, a prediction of the allowed channels of MEDI can be made, along with the kinetic energies of the resulting fragment ions. Starting with the most prevalent energetic ions, \( F^+ \) and \( F^{2+} \), in the simplest scenario, in which all of the fluorine ions in a given channel have the same charge state, we can predict the allowed MEDI channels. This is a reasonable starting point for the analysis, in view of the similarity between the signal for these ions, recorded with polarization parallel and perpendicular to the spectrometer axis (figure 1). The next step in determining the dissociation channel is to find the stages of ionization of the sulphur atom which occur with \( F^+ \) and \( F^{2+} \). The most categorical way to do this would be experimentally, using the covariance mapping technique, developed by the Reading group (Frasinski et al 1989, 1994). However, it is possible to determine the most likely correlations by considering the ionization potentials of the observed fragments. Table 2 gives the zero-field ionization potentials for the sulphur atom and fluorine atom (Moore 1970). First, it should be noted that, because the fluorine ionization potentials

---

Table 2. Ionization potentials of fluorine and sulphur.

<table>
<thead>
<tr>
<th>Species</th>
<th>IP (eV)</th>
<th>Species</th>
<th>IP (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S^+ )</td>
<td>10.36</td>
<td>( F^+ )</td>
<td>17.42</td>
</tr>
<tr>
<td>( S^{2+} )</td>
<td>23.33</td>
<td>( F^{2+} )</td>
<td>34.97</td>
</tr>
<tr>
<td>( S^{4+} )</td>
<td>34.83</td>
<td>( F^{3+} )</td>
<td>62.7</td>
</tr>
<tr>
<td>( S^{5+} )</td>
<td>72.68</td>
<td>( F^{+} )</td>
<td>150.0</td>
</tr>
</tbody>
</table>

Figure 4. Kinetic-energy distributions measured for \( F^+ \), \( F^{2+} \) and \( F^{3+} \). The arrows refer to calculated kinetic energies released for the MEDI channels given in table 3.
Table 3. Possible Coulomb explosion fragmentation channels of SF$_6$ and calculated Coulomb energies for $R_c = 3.51$ Å.

<table>
<thead>
<tr>
<th>Channel</th>
<th>Total energy released (eV)</th>
<th>Fragment energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) SF$_6^{2+}$ → S$^+$ + 6F$^+$</td>
<td>66</td>
<td>F$^+$ (11)</td>
</tr>
<tr>
<td>(2) SF$_6^{4+}$ → S$^{2+}$ + 6F$^+$</td>
<td>90.6</td>
<td>F$^+$ (15.1)</td>
</tr>
<tr>
<td>(3) SF$_6^{14+}$ → S$^{3+}$ + 6F$^{2+}$</td>
<td>262.8</td>
<td>F$^{2+}$ (43.8)</td>
</tr>
<tr>
<td>(4) SF$_6^{15+}$ → S$^{3+}$ + 6F$^{2+}$</td>
<td>312</td>
<td>F$^{2+}$ (52)</td>
</tr>
<tr>
<td>(5) SF$_6^{16+}$ → S$^{4+}$ + 6F$^{2+}$</td>
<td>361.2</td>
<td>F$^{2+}$ (60.2)</td>
</tr>
<tr>
<td>(6) SF$_6^{17+}$ → S$^{3+}$ + 4F$^{2+}$ + 2F$^+$</td>
<td>393.6</td>
<td>F$^{2+}$ (54.1) F$^+$ (88.6)</td>
</tr>
<tr>
<td>(7) SF$_6^{18+}$ → S$^{4+}$ + 4F$^{2+}$ + 2F$^+$</td>
<td>451.2</td>
<td>F$^{2+}$ (62.3) F$^+$ (101)</td>
</tr>
<tr>
<td>(8) SF$_6^{19+}$ → S$^{5+}$ + 4F$^{2+}$ + 2F$^+$</td>
<td>508.6</td>
<td>F$^{2+}$ (70.5) F$^+$ (113.3)</td>
</tr>
</tbody>
</table>

are further apart than the sulphur ionization potentials, two more stages of ionization are present with sulphur than with fluorine. This observation is explained by the fact that the peak intensity varies across the laser focus. Thus, in a region where intensity is just high enough to produce F$^+$, S$^+$ is also produced, while in a region of higher intensity, F$^+$ and S$^2+$ are produced together. Hence, we postulate channels (1) and (2) given in table 3, as the simplest symmetrical channels of MEDI to occur with the production of F$^+$. Table 3 also gives the result of a classical calculation of the fragmentation energy of each of the MEDI channels assuming that the S–F internuclear separation is modified to give the critical Coulomb explosion separation $R_c$, we assume that $C_m = 0.45$. The kinetic energies predicted for channels (1) and (2) are indicated in figure 4 by arrows on the F$^+$ energy distribution and are in reasonable agreement with the position of the shoulder of the distribution. The position of the shoulder is given in table 2 as 17 eV and has been assumed to be approximately the peak of the MEDI kinetic energy distribution. It is possible that S$^{3+}$ could also be produced in a dissociation channel with F$^+$, but the ionization potential of S$^{3+}$ is very close to that of F$^{2+}$ making it much more likely that these ions are produced together. In addition, it can be deduced from table 3 that F$^{2+}$ may be formed in dissociation channels with S$^2+$ and S$^+$ depending on the peak laser intensity. Channels (3)–(5) in table 3 are the simplest symmetrical MEDI channels involving F$^{2+}$. The existence of channel (3) with S$^2+$ can be confirmed from the TOF spectra recorded in the transition between $1.8 \times 10^{13}$ W cm$^{-2}$ and $8 \times 10^{14}$ W cm$^{-2}$ in figure 3(c) and 8 $\times 10^{14}$ W cm$^{-2}$ in figure 3(d). In this transition the F$^{2+}$ and S$^{2+}$ signals have decreased in size relative to the F$^+$ signal, indicating that they are associated. The fact that the reduction in the S$^{2+}$ signal is not as great as the F$^{2+}$ signal indicates that much of S$^{2+}$ is associated with the F$^+$ peak confirming channel (2). As with F$^+$ the kinetic energies calculated for F$^{2+}$ as a result of channels (3)–(5) are in good agreement with the peak of the measured energy distribution.

In accounting for the kinetic energy of the F$^{3+}$ fragment it is necessary to address the question of alignment of the molecule. In the case of F$^+$ and F$^{2+}$ the signals recorded with polarization parallel and perpendicular to the spectrometer axis are very similar, ratios of 1:1 and 3:2 respectively can be deduced. For F$^{3+}$ the anisotropy is much more pronounced having a ratio of signal parallel-to-perpendicular of 4:1. Normand et al (1992b) have shown that anisotropy of fragments resulting from the MEDI of diatomic molecules is due to the alignment of the molecules by the field. Dietrich et al (1993) postulated, that in the case of the diatomic molecule I$_2$, the molecule is ionized at whatever orientation it
happens to lie in the field and is then rotated during dissociation due to the interaction of the field with the induced dipole. However, it is possible that the induced dipole which precedes ionization is responsible for the alignment of the molecule which then ionizes. This process is consistent with the barrier suppression mechanism used by Posthumus et al. (1996) which successfully predicts the critical internuclear separation for ionization. If the process described by Dietrich et al. (1993) is invoked to explain the anisotropy of $F^{3+}$, it would imply that the three axes of SF$_6$ rotate into alignment with the field and become parallel. This is not likely however as it implies that the fluorine ions must come closer together in order for the axes to align and the Coulomb repulsion between the fluorine ions will resist this torque and maintain the orthogonality of the axes. The anisotropy of the $F^{3+}$ ions can however be explained by using the barrier suppression mechanism and the highly symmetric nature of SF$_6$. If distributed with random alignment the SF$_6$ molecule always possess at least one axis which is partially aligned with the field, i.e. it makes an angle with the field of less than 45° and at the same time the molecule has two partially unaligned axes, i.e. they make an angle of more than 45° with the laser field. The molecular interaction potential along the axis which is aligned with the field will experience more distortion at a given intensity than the axes which are unaligned; this will make ionization more likely for the fluorine atoms on the aligned axis. The calculations of Dietrich et al. (1993) estimate that in their experiment this is equivalent to a reduction in the ionization potential, due to a Stark shift, of no more than 15% in the aligned molecules. They state that the difference in ionization potential between aligned and unalined molecules can be compensated for by an increase in the field strength by a factor of 2. Thus, alignment is not crucial in achieving a given stage of ionization provided that the laser field strength and hence the intensity is high enough. This may well be true in the present experiment, where $F^+$ and $F^{2+}$ are concerned, because the peak laser intensity, $7 \times 10^{15}$ W cm$^{-2}$, is at least a factor of eight times higher than the intensity at which these ions appear ($8 \times 10^{14}$ W cm$^{-2}$, figure 3(d)). However, it is not true for the production of $F^{3+}$ where the laser intensity is only just above the appearance intensity and so even a 15% reduction in the ionization potential of $F^{3+}$, due to Stark shift, for those fluorine atoms whose internuclear axis is aligned with the field will be crucial in promoting production of $F^{3+}$. This argument does not require any alignment of the SF$_6$ molecule by the field but distortion and some alignment of the molecule during the MEDI process is likely and will enhance the anisotropy of the $F^{3+}$ ion distribution.

Thus, the simplest MEDI channels which take into account the observed $F^{3+}$ anisotropy are given in table 3 as (6)-(8) and indicated by arrows in figure 4. The kinetic-energy calculations predict the peak of the energy distribution reasonably well but the distribution is wide for $F^{3+}$ and this aspect cannot be reproduced.

5. Conclusions

In this work the MEDI of SF$_6$ has been studied, using TOF mass spectrometry, in order to identify the ions produced at $7 \times 10^{15}$ W cm$^{-2}$ by a 750 nm laser of 60 fs pulse duration. It has been possible to measure the energy distributions of the fluorine fragment ions and establish that the sulphur ions are produced with zero kinetic energy. Considering the zero-field ionization potentials of the observed fragment ions, and observing the TOF mass spectrum and how it varies with laser intensity, we have been able to make predictions of the major channels of MEDI. These predictions give calculated kinetic energies for the fragment ions which are in good agreement with the peak positions of the measured kinetic-energy distributions assuming the same critical internuclear separation $R_c$.

The assumption of a critical internuclear separation at which ionization occurs is
probably the most problematic aspect of this work. We have chosen the value \( C_m = 0.45 \) because of its demonstrated applicability for diatomic ions with light constituents of similar mass to fluorine. It is clear that the formation of \( \text{SF}_6^+ \) must take place near the beginning of the laser pulse since the peak intensity is far above the appearance value, indicated by the appearance of \( \text{SF}_6^+ \) in figure 3, also it is reasonable to expect that the \( \text{SF}_6^+ \) molecular ion, which is known to be in the process of dissociation, should have expanded within the lifetime of the laser pulse to some separation at which further ionization occurs preferentially. Nevertheless, a value of 0.45 for \( C_m \) is quite arbitrary and disregarding any alignment by the field, it is likely that \( R_c \) is different for each axis, depending on its orientation in the field; this would help to explain the wide energy distributions observed in figure 4. The widths of the fluorine kinetic-energy distributions may also be partially due to the existence of asymmetric channels; in this paper we have concentrated on symmetric channels of dissociation since the sulphur fragment ion, kinetic energies peak at zero. However, the energy distributions do possess some width indicating that asymmetric channels can also occur. In future work it would be interesting to confirm experimentally the channels which we have highlighted and identify any asymmetric channels; this could be done by using the covariance mapping technique.

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LETTER TO THE EDITOR

High-intensity femtosecond laser interactions with vibrationally excited CO$_2$

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Abstract. In this work we report the first measurements of the interaction of 60 fs laser pulses at 750 nm with vibrationally excited CO$_2$. Comparison with ground state CO$_2$ is made and enhanced kinetic energies for C$^+$ and C$^{12+}$ observed. These observations are consistent with unusually large bends in the molecule, induced by the laser field.

The interaction of high-intensity laser radiation with simple molecules is an area of active interest; see, for example, Posthumus et al (1996) and references therein. In this letter we are concerned with the fragmentation of the CO$_2$ molecule using laser pulses of 60 fs at 750 nm producing field intensities of $\sim 7 \times 10^{15}$ W cm$^{-2}$. To date all work on laser fragmentation of molecules has been concerned with molecules initially in the lowest vibrational level, but in the present work we have also excited the molecules to upper vibrational levels $(n, n, n)$ and measured the fragmentation spectra. Full dissociation kinetic energy spectra are obtained for the product ions.

The behaviour of ground state CO$_2$ in intense laser radiation has been well characterized experimentally, in the infrared wavelength region, by several groups; Frasinski et al (1994) using the technique of covariance mapping, to identify the allowed channels of multielectron dissociative ionization (MEDI), and also Comaggia et al (1994) and Comaggia (1996), again using covariance mapping, but in this case, to identify bending of the CO$_2$ molecule, during Coulomb explosion.

The laser employed in the present work is a 55 fs system (Langley et al 1994) operating at a centre wavelength of 750 nm with a pulse energy of 60 $\mu$J and a repetition rate of 10 Hz. The incident laser beam enters the vacuum system through a fused silica window which stretches the pulses to 60 fs and is reflection focused using an $f/2$ parabolic mirror into the interaction region giving a near-diffraction-limited spot size, calculated to be 4.2 $\mu$m. The intensity was calculated from the spot size and the pulse energy yielding a peak value of $7 \times 10^{15}$ W cm$^{-2}$ which was confirmed by measuring the charged states of Xe (Augst et al 1989). The laser focus was situated in the central plane equidistant from two parallel
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grids separated by 20 mm, which form the source region of a time-of-flight (TOF) mass spectrometer (Wiley and McLaren 1955). The ions were extracted from the laser focus by applying ±300 V to the grids and then 1002 V before entering the drift tube.

The spectrometer, which has been described previously by Sanderson et al (1997), has a total flight path of 12.53 cm with a pair of microchannel plates of 25 mm diameter used to detect the ions. The apparatus has an ultimate background pressure of around \(4 \times 10^{-10}\) Torr, and the test gas is introduced into the interaction region by a hypodermic needle, the tip of which is situated 10 mm from the laser focus. Vibrationally excited molecules are produced through thermal excitation, by heating the hypodermic needle with a kanthal wire heating element which surrounds it. In a supplementary experiment, a thermocouple was used to determine the temperature, \(T\), of the tip of the needle which was found to be 200°C. Under the experimental conditions employed in our work, the flow rate out from the needle increases as \(T^{1/2}\) and, since the velocity of the molecules also increases as \(T^{1/2}\), the number density in the laser focus is preserved (Lew 1967).

The ion signal is fed through a preamplifier into an EG&G turbo multichannel scalar (MCS). The MCS has a channel width of 5 ns with zero dead time between channels and is capable of counting more than one event per channel.

To ensure that there is no more than a ±5% fluctuation in the energy of the laser pulses entering the experiment, the start pulse to the MCS is gated by monitoring the reflection from the input window with a photodiode. The photodiode pulse height had previously been calibrated against the laser pulse energy and found to be linearly proportional to it. The photodiode pulses are amplified and passed through a single-channel analyser which has a window set to 10% of the desired pulse height. The pulses within the chosen range are used to provide the start pulse for the MCS. The laser pulse shape is also monitored with an autocorrelator so that any drift in pulse width can be detected; the pulse-to-pulse variation in width is less than ±5 fs.

An ionic TOF spectrum obtained for both hot and cold CO\(_2\), with the polarization parallel to the TOF axis, is shown in figure 1. In addition, a spectrum recorded with the heater current on but no CO\(_2\) present is shown in figure 2, in which the prominent contamination features H\(_2\)O\(^+\), OH\(^+\), O\(^+\) and O\(^{2+}\) are detected. These features arise from

![Figure 1. TOF spectrum for CO\(_2\) recorded at room temperature and 200°C. The pulse length is 60 fs, the intensity is \(7 \times 10^{13}\) W cm\(^{-2}\) and the wavelength is 750 nm. The two spectra have been normalized to the number of laser shots.](image-url)
Figure 2. TOF spectrum for background gas recorded at 200°C. The pulse length is 60 fs, the intensity is $7 \times 10^{15}$ W cm$^{-2}$ and the wavelength is 750 nm.

The ionization and dissociative ionization of H$_2$O, evaporated from surfaces by the action of the heater. Apart from these contamination peaks, the differences between the hot and cold CO$_2$ spectra in figure 1 are due to the vibrational excitation of the CO$_2$ molecules.

In the present work the CO$_2$ molecules were non-selectively excited to the vibrational modes of the ground electronic state by resistive heating of the hypodermic needle. At the temperature of 200°C, used in this experiment, 26% of all the molecules are in excited vibrational states, assuming the normal Boltzmann distribution and 19% of the CO$_2$ molecules are in the first excited vibrational level at 83 meV. This level is a bend mode (010) which is non-symmetric in contrast to the ground state symmetric mode (000). In the (010) mode the central carbon atom oscillates in a direction perpendicular to the O–C–O axis, giving a minimum OCO angle $\gamma$ of 156° (Herzburg 1945).

The TOF spectrum recorded at 200°C shows two obvious changes when compared with the room temperature spectrum (see figure 1). Firstly, the amounts of O$^+$ and particularly C$^+$ have increased, while the amounts of the higher stages of ionization have decreased. Secondly, the widths of the C$^+$ and C$^{2+}$ peaks have increased, with the width of the C$^+$ peak more than doubled in the time spectrum. The FWHM of the energy distribution of C$^+$ in figure 3(a), has increased from 1.5 to 5 eV, while the tail has increased to kinetic energies of greater than 30 eV (the C$^+$ energy cannot be measured at higher energies as the C$^+$ peak merges with the O$^{2+}$ TOF peaks at around 30 eV). In figure 3(b) the FWHM of C$^{2+}$ has increased from 2.5 to 3.5 eV and a high-energy tail is visible up to 30 eV. It should be noted that the backward O$^{3+}$ peak has been centred on the C$^{2+}$ feature. However, this overlap does not contribute to the increased width of the C$^{2+}$ feature as the resolved forward O$^{3+}$ peak clearly has the same width for CO$_2$ molecules both in the ground and excited states. Modifications to the oxygen ion kinetic energies are small; in figure 4(a) the O$^+$ ion kinetic energy distribution, derived from the forward part of the TOF distribution at 200°C, shows more O$^+$ overall than in the room temperature spectrum, with slightly more enhancement at low kinetic energies. For O$^{2+}$ and O$^{3+}$ in figures 4(b) and (c), respectively, the overall signal is decreased, but less so at the low kinetic energies.

The modification to the TOF spectra are primarily associated with the carbon ions, and this is the best indicator of how the laser field has interacted with the excited CO$_2$ molecule, predominately in the (010) mode. When initially in the ground state mode the CO$_2$ molecule
will preferentially distort along the O–C–O axis, rotate by virtue of the induced moment and dissociate with the O–C–O axis parallel to the laser polarization direction. Cornaggia (1996) has shown that for CO$_2$ initially in the ground state the $O^+ + C^+ + O^+$ channel is aligned with the laser field such that a model distribution of angles $\theta$ (the angle which the O–O axis makes with the laser field), which is peaked at 0° and extends to 60° is a good fit to their covariance map data. However, in the case of the initially vibrationally excited CO$_2$ molecule it is likely that the non-symmetric bending vibration, which has a permanent dipole moment perpendicular to the O–O axis, allows the molecule to couple more strongly with the laser field, aligning the O–O axis perpendicular to the laser polarization ($\theta = 90°$). If this is the case the CO$_2$ molecule will then tend to bend further, decreasing the bend angle $\gamma$. When Coulomb explosion of the sharply bent molecule takes place, conservation of momentum causes the carbon ion to be ejected with a large velocity parallel to the laser field direction, and the oxygen ions to be ejected with a small velocity parallel to the laser polarization direction. The result, as seen in figure 1, is a modification to the TOF spectrum, recorded with the laser polarization parallel to the spectrometer axis, in the form of wider carbon ion peaks but with no significant change to the oxygen peaks.

To account for the kinetic energies of the C$^+$ ions in figure 3(a) it is necessary to determine the degree of bend induced by the laser field. We have assumed that $\theta = 90°$, the equilibrium C–O bond length of 1.16 Å is constant, and that the C$^+$ ions result from the
O\(^+\) + C\(^+\) + O\(^+\) channel, the angle \(\gamma\) has been varied and the resulting Coulomb energies calculated. For \(\gamma = 90^\circ\) it is possible to generate a C\(^+\) energy of 13.7 eV, which is in the tail of the measured C\(^+\) energy distribution (figure 3(a)). This reaction also produces O\(^+\) ions which have a kinetic energy of only 2.6 eV. Evidence to support an enhancement to the bend of an initially bent molecule, due to the laser field, can also be found in an experiment by Cornaggia et al. (1996) performed on SO\(_2\) for which \(\gamma = 120^\circ\) initially. It is possible to deduce the kinetic energy of the S\(^+\) and O\(^+\) ions from the TOF peaks reproduced in their paper. The covariance island, shown in their paper allows us to measure these kinetic energies for \(\theta = 90^\circ\), where the S\(^+\) energy is found to be 5.5 eV and the O\(^+\) energy 3 eV. We have modelled this fragmentation, as with CO\(_2\) and find a good fit with \(\gamma = 90^\circ\), which gives an S\(^+\) energy of 5.7 eV and an O\(^+\) energy of 2.8 eV. This represents an enhancement in \(\gamma\) of 30° at \(\theta = 90^\circ\). We conclude that ranges of \(\gamma\) exist for both SO\(_2\) and excited CO\(_2\) which are a minimum when \(\theta = 90^\circ\).

Clearly, the C\(^{2+}\) and C\(^{3+}\) ions are much less affected by the vibrational excitation of CO\(_2\) as only a residual high-energy tail is present. With \(\gamma\) and \(\theta\) set to 90°, the C\(^{2+}\) energy calculated is 55 eV from the O\(^{2+}\) + C\(^{2+}\) + O\(^{2+}\) channel, which is higher than observed. It seems that the higher stages of ionization result from only the well aligned molecules.
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This is probably because, for the higher channels, good alignment of the O–C–O axis with the field is required to remove the electrons. The consequence of this is that the bent molecules, which are not well aligned, preferentially produce lower stages of ionization and this accounts for the increase in the C⁺ and O⁺ signal and the depletion of the higher stages of ionization in the excited CO₂ TOF spectrum.

This work has been an investigation of laser-induced field ionization of CO₂, both in its ground and excited state configurations, with observation of the excited CO₂ molecule fragmentation obtained for the first time. The results obtained with CO₂ heated to 200°C indicate that for the lower stages of ionization bending of the molecule is enhanced during the fragmentation process and the angular orientation distribution is extended to $\theta = 90^\circ$.

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LETTER TO THE EDITOR

Alignment and bending of CO$_2$ by intense femtosecond laser pulses

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Abstract. We report on direct measurements of the angular distributions of CO$_2$ fragment ions produced in interactions with 60 fs laser pulses at 750 nm. These distributions show dramatically the bent nature of the dissociating molecule, and allow observation of the alignment of the different dissociation channels. It is found that for the lowest channel of multielectron dissociative ionization, alignment parallel to the laser field is preferred, but orientation perpendicular to the laser field direction is allowed. For the higher channels orientation perpendicular to the field is not allowed. Where possible the distributions measured are compared with those deduced from fits to the double-correlation data of Cornaggia.

The process by which a molecule is multiply ionized and dissociates in the field of a high-intensity short pulse laser has been the subject of much work recently (Codling and Frasinski 1993). It has emerged that molecules stretch and rotate in the laser field and some evidence has shown that triatomic molecules also bend in the laser field (Cornaggia 1996) with some fragments displaying spatial alignment in the laser field (Bhardwaj et al 1997). In this work direct observations of the consequences of induced bending of the CO$_2$ molecule are made using an angular measurement technique.

The laser employed in the present work is a 55 fs system (Langley et al 1994) operating at a centre wavelength of 750 nm with a pulse energy of 60 µJ and a repetition rate of 10 Hz. The incident laser beam enters the vacuum system through a fused silica window which stretches the pulses to 60 fs and is reflection focused using an f/2 parabolic mirror into the interaction region giving a nearly diffraction-limited spot size, calculated to be 4.2 µm. The intensity was calculated from the spot size and the pulse energy, yielding a peak value of $7 \times 10^{15}$ W cm$^{-2}$. The laser polarization direction was controlled by a half-wave plate. The laser focus was situated in a central plane equidistant from two parallel grids separated by 20 mm, which formed the source region of a Wiley–McLaren-type time-of-flight (TOF) mass spectrometer (Wiley and McLaren 1955). The spectrometer, which has been described previously by Sanderson et al (1997), has a total flight path of 12.53 cm with a pair of microchannel plates of 25 mm diameter used to detect the ions. In order to measure angular distributions a 2 mm diameter aperture was placed directly in front of the channel plates. The apparatus has an ultimate background pressure of $4 \times 10^{-10}$ Torr and the test gas is introduced into the interaction region by a hypodermic needle, the tip of which is situated...
10 mm from the laser focus. In this work the molecules were produced only in the ground vibrational state.

The ion signal is fed through a preamplifier into an EG&G turbo multichannel scalar (MCS). The MCS has a channel width of 5 ns with zero dead time between channels and is capable of counting more than one event per channel.

To ensure that there is no more than a 10% fluctuation in the energy of the laser pulses entering the experiment, the start pulse to the MCS, obtained by monitoring the reflection from the input window with a photodiode, is gated. The photodiode pulse height has previously been calibrated against the laser energy and found to be linearly proportional to it. The photodiode pulses are amplified and passed through a single-channel analyser which has a window set to ±5% of the desired pulse height. The pulses which are within the chosen range are used to provide the start pulse for the MCS. The laser pulse shape is also monitored with an autocorrelator so that any drift in pulse width can be detected; the pulse-to-pulse variation in width is less than ±5 fs. In order to prevent any systematic effects due to small drifts in intensity the polarization direction was varied in a random sequence, over more than one quadrant. Each TOF spectrum was built up over 10 000 laser pulses.

To date two techniques have been used to make direct angular measurements: first, TOF was used by Dietrich et al (1993) and Normand et al (1992), employing a system similar to the present experimental set-up. In each case the angular resolution of the experiment was set by the size of an aperture either in front of the detector or in the extraction region. In this method the extraction field established between the two parallel grids plays a part in setting the detection efficiency of the TOF spectrometer. A second technique used by Kumar et al (1994) utilizes an apparatus consisting of a field-free region between the two parallel grids followed by an aperture and an extraction region leading to a quadrupole mass spectrometer. In this method the angular resolution is set only by the aperture size. The major advantage of the quadrupole system is that the angular resolution is independent of the initial kinetic energy of the ion. Resolutions of a few degrees have been achieved using this method, allowing the observation of pendular motion in the angular distribution of some triatomic molecules in picosecond laser pulses. No such observations have been observed using the first method. Nevertheless, certain advantages are apparent in using TOF to measure angular distributions. Firstly, for a given angle, the signal from all ions arising from a laser pulse can be recorded in the form of a spectrum. This allows experimental conditions to be kept constant during the acquisition of different ions and saves time in data acquisition. Second, and most importantly, fragment ions of the same species which result from different channels of multi-electron dissociative ionization (MEDI) can be distinguished by their flight times.

Figure 1 shows how the angular acceptance of the detector varies for the O+ and O2+ ions over a range of kinetic energies. The acceptance angle is simply twice the maximum initial angle which the ion trajectory can make with the TOF axis and be detected. The angular acceptance is a maximum of 180° for ions of nearly zero kinetic energy, but the combination of aperture size and extraction fields used have been chosen to give an acceptance angle of less than 8° for ion fragments of energy greater than 2 eV.

Figures 2(a) and (b) show the magnitude of the C+ and O+ ion signals as a function of the angle θ between the laser polarization direction and the detector axis. The data were recorded in two quadrants and the data from each quadrant were reflected into the other three quadrants. Some disparity in the signal strength between the two quadrants in the case of the C+ ion leads to the appearance of a double line in figure 2(a). This difference in signal strength is probably due to a small lateral offset of the laser focus from the spectrometer axis. O+ ions from predominantly the (1, 1, 1) channel have been chosen, by selecting only those
ions within a specific kinetic energy range as determined from a supplementary coincidence experiment using the covariance mapping technique (Frasinski et al 1989). In the present case O\(^+\) ions in the range 4-10 eV were selected, the peak in the C\(^+\)-O\(^+\) correlation being 7 eV. What is striking is the orthogonality of the two distributions with the trajectory of the C\(^+\) ions maximum when the laser polarization direction is perpendicular to the TOF axis and the trajectory of the O\(^+\) ions maximum when the laser polarization is parallel to the TOF axis.
The implications of this pair of distributions are clear, firstly the CO\textsubscript{2} molecules which give rise to the (1, 1, 1) channel have their O–O axis strongly aligned with the laser field direction, giving rise to an O\textsuperscript{+} ion distribution peaked along the polarization direction and secondly the molecules are bent at the time of the Coulomb explosion giving the C\textsuperscript{+} ions a distribution of trajectories peaked perpendicular to the field. This pattern has been previously observed indirectly by Cornaggia (1996), using the double-correlation technique in an experiment using a similar wavelength (750 nm), but with longer pulse duration (150 fs).

In this work our primary concern has been to interpret the angular distributions of the oxygen ions, particularly O\textsuperscript{+}. Considering the O\textsuperscript{+} angular distribution in more detail by displaying the O\textsuperscript{+} ions from the (1, 1, 1) channel on a conventional plot, figure 3, it can be seen that the angular distribution is peaked around 0° with a minimum at around 40° and a secondary maximum at larger angles around 90°. Figure 3 shows two fits to the experimental data: a triangular fit and an $A \cos^n(\theta)$ fit; the triangular distribution was used by Cornaggia (1996) to reproduce the major feature in the double-correlation map, but not the weaker correlations which correspond to the present data detected at large angles up to 90°. Clearly, the ions from the (1, 1, 1) channel fall into two distinct distributions. We have fitted the data near to 0° with an $A \cos^n(\theta)$ function as used previously by Dietrich et al (1993) and Thompson et al (1997), to enable direct comparison of the widths of the distributions as indicated by the exponent $n$. We do not claim any special physical significance for this type of distribution but its continuous functional form makes it clearly more physical than a triangular distribution and since the higher ionization channels, for example, (2, 2, 2), occur when the molecule is more completely aligned with the laser polarization direction this will be reflected in the $n$ value. Table 1 shows values of $n$ and $A$ obtained from the least-squares fitted distributions for channels (1, 1, 1), (1, 2, 1), (2, 2, 2) and (2, 3, 2). Some of the data points close to 0° which do not lie on any smooth curve have not been included.
Table 1. Parameters derived from the least-squares fit of $A \cos^6(\theta)$ to the measured angular distributions.

<table>
<thead>
<tr>
<th>Channel</th>
<th>$n$</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>12</td>
<td>0.0028</td>
</tr>
<tr>
<td>121</td>
<td>13</td>
<td>0.0002</td>
</tr>
<tr>
<td>222</td>
<td>15</td>
<td>0.0017</td>
</tr>
<tr>
<td>232</td>
<td>16</td>
<td>0.0014</td>
</tr>
</tbody>
</table>

as points in the fit. This means that the fitted distributions may underestimate the value of $n$, nevertheless the $n$ value of 12 for the (1, 1, 1) channel is high and this indicates that the molecule is reoriented by the laser field (Giusti-Suzor et al. 1995). This value of $n = 12$ compares with the value of $n = 20$ for the (1, 1) channel of H$_2$ (Thompson et al. 1997) and $n = 3$ for the (1, 1) channel of I$_2$ (Dietrich et al. 1993) for which molecular reorientation is invoked as an explanation in both cases.

If a molecule is in one of the rotational levels populated at room temperature with a period of the order of picoseconds, then there is no possibility that significant reorientation can take place on the time scale of the current experiment (0–100 fs). However, when the CO$_2$ molecule is subjected to the extreme electric field of the laser ($2 \times 10^8$ V cm$^{-1}$) it couples with the molecular polarizability ($2.9 \times 10^{-24}$ cm$^3$) to induce a dipole and a torque sufficient to produce a classical molecular rotational period of around 15 fs, then molecular reorientation is possible dynamically. However, the interaction dynamics of the laser and molecule become nonlinear before any classical oscillation can develop and dissociative ionization can commence while the molecule is reorientating.

The induced dipole parallel to the CO$_2$ axis is clearly dominant, reorientating the majority of the bent molecules such that the O–O axis aligns with the laser field and the bond stretches before dissociation (Frasinski et al. 1994, Cornaggia et al. 1994). However, this process does not explain the second O$^+$ distribution peaked at large angles in the (1, 1, 1) channel.

The interaction potential $V_a(\theta)$ of a molecule with polarizability components parallel $\alpha_{||}$ and perpendicular $\alpha_\perp$ to the internuclear axis is given by the expression

$$V_a(\theta) = -\frac{1}{2} e^2 (\alpha_{||} \cos^2(\theta) + \alpha_\perp \sin^2 \theta)$$

where $\theta$ is the orientation of the internuclear axis to the laser field $\epsilon$ (Friedrich and Herschbach 1995). The function $V_a(\theta)$ is dependent on the ratio $\alpha_{||} : \alpha_\perp$ such that if this ratio is typical for a linear molecule 2 : 1, then the function has only one minimum at $\theta = 0^\circ$. This concurs with the main distribution which is observed for the (1, 1, 1) channel. If the ratio $\alpha_{||} : \alpha_\perp$ were to change, as would happen if the molecule bends and stretches in the laser field, then it would be possible to explain the second maximum in the observed O$^+$ distribution at $\theta = 90^\circ$ as due to a second minimum in the $V_a(\theta)$ function. Bhardwaj et al. (1997) using a 35 ps laser pulse with intensity of $10^{13}$ W cm$^{-2}$ have observed that for the O$^+$ fragment channel of H$_2$O the distribution displays two maxima at $\theta = 0^\circ$ and $90^\circ$ superimposed on an isotropic background. The isotropy is explained as the result of $\alpha_{||}$ and $\alpha_\perp$ being of similar magnitude, such that the parallel and perpendicular torques cancel each other out, but the double peak is not commented on. It seems possible that it results from the variability of $\alpha_{||}$ and $\alpha_\perp$ with alignment, as the bend angle of H$_2$O is modified by the laser field, allowing reorientation of molecules away from as well as towards the laser polarization direction. This process seems much more likely to occur for H$_2$O than for CO$_2$, because $\alpha_{||}$ and $\alpha_\perp$ are already quite close in magnitude (Bhardwaj et al. 1997), where as
for an initially linear molecule $\alpha_\parallel$ is typically twice $\alpha_\perp$. However, this reorientation process does concur well with the present result.

The physics of picosecond laser pulse interactions with molecules is quantitatively different from that produced by femtosecond pulses, the major difference being the much higher intensities present in the femtosecond regime. This means that many higher stages of ionization can be produced in the latter case, and the competing processes must be distinguished. Furthermore, the laser focus consists of regions of different intensity and the spatial distribution of the many ionization channels within the focus is an active field of research, in the case of atomic targets (Hansch et al 1996). However, with molecular targets, the angle of orientation may play an important role in determining the distribution of a given channel and blur the regions in which different ions are produced. The field ionization model implies that the probability of producing say the (1,1,1) channel in a region of uniform electric field, depends on the angle which the molecular axis makes with the laser field direction, being a maximum when the axis and field are parallel, and a minimum when they are perpendicular (Posthumus et al 1998). This means that in figure 3 the two distributions must result from ionization in regions of different field strength. The main distribution around $0^\circ$ will result from a region of field strength where good alignment can produce the (1,1,1) channel, but no higher channel. In this region any molecules orientated at large angles to the field will only produce lower channels of ionization. The distribution at high angles, however, must result from a region of much higher intensity where poor alignment with the field is sufficient to produce the (1,1,1) channel, and good alignment with the field results in higher ionization channels. At lower laser intensity this second distribution should disappear, unfortunately this could not be investigated experimentally as signal conditions were poor and to lower the intensity further was not feasible.

![Figure 4](image-url)
Figure 5. Angular distribution of O\(^{2+}\) from predominantly the (2,2,2) channel. When \(\theta\) is zero the TOF axis is parallel to the laser polarization direction. The curve is an \(A \cos(\theta)^n\) least-squares fit (see table 1) and the straight lines are the triangular distribution derived from the double-correlation map by Cornaggia (1996).

We have previously deduced indirectly (Sanderson et al 1998) that in the case of initially vibrationally excited CO\(_2\) molecules, a proportion of which are bent, more CO\(_2\) molecules in the (1,1,1) channel are produced with their alignment non-parallel to the laser field direction, i.e. with high \(\theta\). We also noted that the number of C\(^+\) and O\(^+\) ions increased overall, whereas the higher ionization stages decreased. We suggested that this was because reorientation of the molecule is more difficult to achieve with the initially bent structure, due to an increase in the perpendicular polarizability and so the fuller alignment with the field, which is essential in producing the higher stages of ionization such as (2,2,2) and (2,3,2), does not occur as often. Both of these phenomena are reflected in the present results, the values of \(n\) for the higher channels increase, and the second distribution at large angles is first reduced for O\(^+\) ions from the (1,2,1) channel, in figure 4 and disappeared for the O\(^{2+}\) ions from the (2,2,2) channel in figure 5. It is also notable that the fitted distributions in figures 4 and 5 are in good agreement with the triangular distribution devised by Cornaggia (1996), and that for these channels no high-angle correlations were observed.

In conclusion, the direct measurements of the angular distributions of the carbon and oxygen ions show clearly the orthogonal trajectories which the C\(^+\) and O\(^+\) ions possess. Such angular distributions can only result when a molecule is bent, confirming the deduction of Cornaggia (1996). The progressive alignment of the molecules with the polarization direction necessary for the higher stages of ionization to occur is indicated, by the increase in \(n\) value associated with the degree of ionization in a channel. Finally, there is some evidence that molecules may be rotated away from the laser polarization direction, in the region of highest intensity, a process which requires further investigation.

This work was supported by EPSRC.
References

Appendix 7.4

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Geometry modifications and alignment of H$_2$O in an intense femtosecond laser pulse

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The Coulomb explosion of H$_2$O in laser pulses of 50 fs and intensity of 3×10$^{15}$ W/cm$^2$ has been investigated using an ion momentum-imaging technique to determine the shape of the exploding molecule. The molecule is found to straighten substantially during the ionization process with the bend distribution at a maximum between 130° and 180°.

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Modifications to the structure of a small molecule during laser-induced Coulomb explosion is an active area of interest at present. Experiments have shown that the bond lengths of polyatomic molecules as large as SF$_6$ have been found to support bending of both the ground state [2,3,4] and vibrationally excited [5] CO$_2$ molecule, and straightening of the initially bent SO$_2$ molecule [6]. A more recent experiment indicated that SO$_2$ retains its bent structure [7] for high ionization channels. In the present experiment we use a momentum-imaging technique developed by Hishikawa et al. [7] to examine the modification to the initially bent H$_2$O molecule in a 50-fs laser pulse of peak intensity 3×10$^{15}$ W/cm$^2$.

The 790-nm, 10-Hz laser used in the present experiment has been modified from that used in earlier studies [1,4,5]. The incident laser beam enters the vacuum system, which has a base pressure of 10$^{-9}$ Torr, through a fused silica window and is reflected focused using an f/5 spherical mirror into the interaction region, which gives a near-diffraction-limited Gaussian spot radius, calculated to be 2.5 μm. The intensity was derived from the spot size and the pulse energy of 900 μJ per pulse at 3×10$^{15}$ W/cm$^2$. The direction of the laser polarization was controlled using a half-wave plate. The laser focus was situated in a central plane equidistant from two parallel grids separated by 20 mm, which formed the source region of a Wiley-McLaren-type time-of-flight (TOF) mass spectrometer [8], in which a 3-mm aperture was placed in front of the microchannel plates [4]. During the experiment the target gas pressure rose to 10$^{-7}$ Torr and was maintained constant to provide a clear ion image. The pulses were monitored as previously [4] in order to minimize the effect of energy fluctuations. The polarization was rotated in 2° steps and a TOF spectrum was recorded at each step. Only one hundred laser pulses were needed to build up each spectrum and so a two-dimensional matrix of TOF spectra from 0° to 360° could be built up in approximately 30 min. The intensity distribution of an ion as a function of momentum, $I(P)$, is derived for each TOF spectrum, using the formula $P = e q ΔT$, where $q$ is the ion charge, $e$ is the extraction field strength, and $ΔT$ is the flight time relative to the known flight time of an ion with zero initial momentum. A momentum map is then created by combining the distributions in polar form to give the signal strength as a function of momentum and angle with respect to the laser polarization direction.

Figures 1(a)–1(c) show momentum maps [7] of the observed atomic fragment ions, H$^+$, O$^+$, and O$^{2+}$ constructed from data recorded at 2° intervals from 0° to 360°. The vertical axis is parallel to the laser polarization direction. Clear information can be gained from these plots. Figure 1(a) shows a low-momentum island (<10×10$^3$ amu ms$^{-1}$) con-
sisting of ions from the H\(^+\)+OH (1,0) channel. The island is circular, indicating that the angular distribution of these ions is isotropic. The crescent-shaped islands, which consist of ions from the Coulomb channels (1,1,1) and (1,2,1), have a wide angular distribution, but are not isotropic. The gray intensity scale shows that these islands have their highest values at angles close to 0° and 180°, which indicates that the Coulomb explosions result from H\(_2\)O molecules in which a certain amount of alignment exists between the H-H axis and the laser polarization direction. We have fitted a function of the form \(A \cos^2 \theta\) to the H\(^+\) angular distribution, at a momentum of \(40 \times 10^4\) amu ms\(^{-1}\), which is close to the highest point on the island (at 0° and 180°). The least-squares fit gives a value of \(n = 4.5\), which compares with \(n = 12\) for the (1,1,1) channel of CO\(_2\) at the same laser intensity [4]. We can try to explain the observations of both the low- and high-momentum hydrogen fragments by considering a number of important results.

Recent experiments with laser pulses of less than 100 fs and intensity greater than 10\(^{14}\) W/cm\(^2\) have shown that the angular distributions of fragments from light diatomic molecules cannot be explained simply by the higher ionization rate of molecules, which are initially aligned with the laser field [9,10]. This indicates that the laser field reorients light diatomic molecules on a femtosecond time scale. By contrast it was found that the massive \(I_2\) molecule could not be reoriented on such a short time scale. The H\(_2\)O molecule is light and so it is reasonable to assume that the origin of the angular distribution, observed here, is the reorientation of the H\(_2\)O molecule by the laser field. The static-field-induced dipole strengths parallel and perpendicular to the H-H axis have recently been calculated for a range of field strengths [11]. These calculations suggest that at low laser intensity (=10\(^{13}\) W/cm\(^2\)), the torques on the molecule associated with these dipoles are roughly equal and opposite, so that the molecule is not reoriented. The angular distributions of H\(^+\) ions, most probably from the (1,0) channel, were measured in that work and found to be isotropic. This observation is confirmed in the present work, as the low-momentum H\(^+\) ions must originate from a region within the focal spot where the intensity is low enough to result in only single ionization channels such as (1,0). The calculations further showed that at higher intensities, the parallel-induced dipole becomes dominant and so the molecule should be rotated, such that the H-H axis aligns with the laser field. This prediction is confirmed by the present result. The effect of opposing torques should reduce the amount of reorientation experienced by the molecule in comparison with more linear molecules such as CO\(_2\), leading to a lower value of \(n\) as observed here. Furthermore, the bent nature of H\(_2\)O is important in widening the angular distribution of the Coulomb channel in a very simple way. If the H-H axis is completely aligned with the polarization direction, the trajectories of the H\(^+\) ions cannot be along the polarization direction, because of the repulsion from the laterally offset oxygen ion. The bent nature of H\(_2\)O is deducible from Figs. 1(b) and 1(c) in which the O\(^+\) and O\(^{2+}\) momentum plots are elliptical. In both cases the major axis of the ellipse is orientated at 90° to the laser polarization direction. This indicates that the molecules aligned with the H-H axis along the polarization direction repel the central oxygen ion at right angles to the polarization direction; this is only possible from a bent geometry.

Further information about the molecular geometry can be extracted from the momentum maps, but first it is necessary to correct the data for the effect of the variation of detector acceptance angle with ion momentum. This variation has the most effect on the oxygen ion maps in Figs. 1(b) and 1(c), because the momenta of the oxygen fragments are small, and so the acceptance angle becomes large, reaching \(\pi/2\) for momenta close to zero. This means that the ion distributions appear more isotropic than is physically the case. Figure 2 shows the geometry, which must be considered for the correction procedure applied to each momentum point \(P\) on the map. In Fig. 2 the signal \(S\) measured at a particular momentum \(P\) is proportional to the momentum surface area \(A\), defined by \(m(\tan \alpha)^2\), where \(\alpha\) is the acceptance angle of the most energetic ion, which can be detected with momentum \(P/(\cos \alpha)\) and which can be calculated from the experimental geometry. The measured signal is divided by the factor \(\pi \sin^2(\alpha)\), which is analogous to a solid angle correction. A fuller discussion of this and other correction procedures will be given elsewhere.

Figures 3(a)–3(c) show the angular distributions of H\(^+\), O\(^+\), and O\(^{2+}\), respectively, after a correction for the variation of acceptance angle. In Fig. 3(a) the central island is now not visible, but the Coulomb islands have not been greatly altered, as their momentum is high. The major difference is in Figs. 3(b) and 3(c) where removing the false isotropy has transformed the elliptical islands into "bow-tie"-shaped islands. It is now possible to use the three corrected maps to deduce the geometry of the exploding molecule, by comparing them with maps derived from a Monte Carlo simulation of the Coulomb explosion of the H\(_2\)O molecule from a distribution of geometries. A similar technique has been used previously [3] to determine molecular geometry from the islands of a double correlation map. In the present simulation, three independent distributions are chosen to represent the O—H bond length \(R\), the H—O=H bond angle \(\theta\), and the alignment angle \(\phi\) between the H-H axis and the laser polarization direction. The distributions used are either triangles or trapeziums for ease of calculation. The simulated O\(^+\) map was derived from a set of \(R\), \(\theta\), and \(\phi\) distributions in which the molecule was allowed to explode into the (1,1,1) channel and the O\(^{2+}\) map was derived from a set of distributions in which the molecule exploded into the (1,2,1) channel. The simulated H\(^+\) map contains contributions from both channels, weighted in accordance with the magnitudes

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of the O' and O2+ ion intensities of Fig. 3. The simulated maps were individually normalized so that they could be compared with the experimental maps. The initial distributions chosen were consistent with the geometry of the neutral molecule, i.e., the $\theta$ distribution peaking at 104° and the $R$ distribution peaking at 0.96 Å. These were not found to give a good agreement with the experimental map, and so were varied until the best agreement was found. Figures 4(a)–4(c) show a comparison between the experimentally derived and the best-simulated momentum maps. The general agreement is good, with the simulated maps reproducing the shape of the islands and the positions of the highest ion signal in the experimental maps.

Figures 5(a)–5(e) show the derived distributions for $R$, $\phi$, and $\theta$. For both channels, the $R$ distribution was found to peak at 2 Å, in good agreement with the critical distance theory [12,13]. The alignment distribution $\phi$ narrows with increasing ionization channel as expected [4]. This is for two reasons: better alignment is needed between the molecule and the field to produce the higher ionization channel; and the greater field strength, which produces the higher channel, also gives rise to more reorientation. Triangular alignment distributions with full width at half maximum of 60° and 40° were derived to describe the (1,1,1) and (1,2,1) channels of CO$_2$ [3], as compared to 70° and 60°, respectively, in the present work. The results are therefore consistent with reorientation of H$_2$O, but to a lesser extent in H$_2$O than in CO$_2$, due to competition between the parallel and perpendicular torques. The maximum in the bond angle $\theta$ distribution is at 130° for the (1,1,1) channel and 140° for the (1,2,1) channel. This compares with a most probable angle of 104° for the neutral molecule; even more striking is the fact that the bend angle distributions saturate at these values. Figure 5(d) also shows a comparison with the angle between the H$^+$ trajectories, calculated with a multiconfigurational self-consistent-field technique [14] for dissociating H$_2$O$^+$ and H$_2$O$^+$ excited by highly charged ion impact. These distributions describe the molecular ion geometries well, but the bond angles cannot directly be derived from them, as the dissociation is not completely Coulombic. Nevertheless, the dissociation is close to Coulombic, the $\theta$ distributions are a good approximation to the natural bond angle distributions, and they show a low probability for large angles. In the present work the observation of high probabilities for large bond angles, between 130° and 180°, strongly indicates that the molecules have been straightened in the laser field. The phenomenon responsible for this straightening of the molecule may be bond angle softening [15], tentative evidence for which has been found in the photoelectron spectrum of H$_2$O at 532 nm. Figure 6 shows the interaction potential as a function of $\theta$ for the H$_2$O$^+$ ion with the A $^2B_1$ state lowered by the photon energy of 1.6 eV. This makes the crossing positions close to the centers of the wells of the $^2B_1$ ground state, and close to the most probable angle for H$_2$O$^+$. 

FIG. 3. Momentum maps after correction for the finite collection angle of the detector.

FIG. 4. Comparison between experimental (EXP) and simulated (SIM) momentum maps.
FIG. 5. Distributions of the bond length $R$, alignment angle $\phi$, and bend angle $\beta$ used to generate the simulated map in Fig. 4. Also shown are the $\theta_e$ distributions calculated by Werner et al. [14]. See the text for a discussion of the single-photon process, which allows the molecule to access large bond angles, in the present experiment.

which is $120^\circ$. The process of bond angle softening occurs by a single-photon transition from the ground state onto the $\tilde{A}^2A_1$ state; the molecule then begins a large-amplitude oscillation to the other crossing, where it emits a photon and returns to the ground state. The time scale for this motion is comparable to the rise time of the laser pulse. If the molecule is ionized near the start of the laser pulse, which is likely, then there is enough time for the ion to undergo this bending process before the peak intensity is reached, and Coulomb explosion takes place. The bend angle distribution would be modified in this process, increasing the importance of large angles as observed.

In conclusion, using high-intensity femtosecond laser pulses, we have been able to excite the $\text{H}_2\text{O}^+$ molecule to high vibrational levels through a single-photon, bond angle softening process, and observe the resulting nuclear motion, through Coulomb explosion, using a momentum-mapping technique. This technique has also revealed the stretching of the bonds, before Coulomb explosion, consistent with enhanced ionization and alignment of the fragment ions, consistent with the reorientation of the molecule in the laser field. Further theoretical studies of the bond angle softening process in a high-intensity laser pulse would be beneficial.

LETTER TO THE EDITOR

Sub-pulsedlength time resolution of bond softening and Coulomb explosion using polarization control of laser-induced alignment

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Abstract. Two 50 fs laser pulses with orthogonal laser E-fields are superposed with a time delay of less than the pulse duration, producing a single peaked pulse with a continuously varying ratio between the horizontal and vertical laser E-fields. Since the ejection angle of H⁺ fragments in the multiphoton dissociative ionization of H₂ is dependent upon the laser polarization, this technique can be used to resolve events on a sub-pulse timescale. Using focused intensities of about 5 x 10¹⁶ W cm⁻², the results show that Coulomb explosion of H₂ occurs primarily on the rising edge of the pulse. Bond-softening peaks, however, are associated with the falling edge, in agreement with the earlier notion that only then can enhanced ionization at the critical internuclear separation be avoided. The surprisingly small energy spread of the bond-softening peaks, as observed in a recent high-resolution study, can be explained in a consistent manner.

Recent progress in the understanding of multiphoton dissociative ionization of molecules has emphasized the significance of the interplay between ionization and dissociation. It has been recognized that the phenomenon of enhanced ionization at the critical internuclear separation, Rc, is fundamental to the Coulomb explosion process [1] and, in particular, is required to explain the behaviour of H₂ in short-pulsed, intense laser fields [2, 3]. More recently, the effect of enhanced ionization on angular distributions and, consequently, on laser-induced alignment has been appreciated [4-6].

From experiment [3, 7] it is evident that the progressive fragmentation channels of H₂ (H₂⁺⁺ + e⁻, H⁺ + H⁺ + e⁻ and H⁺ + H⁺ + 2e⁻) appear sequentially, as a function of increasing laser intensity. The absence of conspicuous ‘shoulders’ in the ion yield curves suggests that non-sequential processes are of secondary importance. Nevertheless, the appearance intensities of the channels fall within a very small range.

The ion yield curves can be reproduced by simulating the expansion of the focal volume and assigning appropriate population probabilities to the channels [7]. The results for ultra-short Ti:sapphire laser pulses at the fundamental wavelength have not been published previously and are presented in figure 1. Although such probabilities can be related to a simple model [7], it is important to realize that the population distributions are defined by the experimental data.
The curves of figure 1 reveal that if the laser is focused to a sufficiently high peak intensity, e.g. $4 \times 10^{14}$ W cm$^{-2}$, all molecules in the centre of the focus reach the $\text{H}^+$ + $\text{H}$ channel. The intermediate channels, $\text{H}_2^+$ and $\text{H} + \text{H}^+$ or (0, 1), are only produced outside the centre of the focus, in the shell extending from about $1-3 \times 10^{14}$ W cm$^{-2}$. The constitution of this shell is surprising, since the relative populations of these intermediate channels never exceed 25%. In fact, at an intensity of just under $2 \times 10^{14}$ W cm$^{-2}$, all four channels, including the neutral, coexist in comparable numbers. Further out, at intensities below $1 \times 10^{14}$ W cm$^{-2}$, most $\text{H}_2$ molecules remain stable. The remarkable overlap of all channels in the active shell is explained by the stability of the neutral molecule [7]. Once $\text{H}_2$ is ionized, the other processes occur sequentially with a significant probability.

Multiphoton transition rates increase rapidly with laser intensity and since the (1, 1) curve in figure 1 saturates at 100% around $3 \times 10^{14}$ W cm$^{-2}$, we believe that for higher intensities, Coulomb explosion must inevitably occur on the rising edge of the laser pulse. On the other hand, the (0, 1) channel peaks at the 25% level, the reason being that the dissociating molecule easily ionizes further when it reaches $R_e$. We suggest, therefore, that a molecule in the (0, 1) channel is less likely to experience the next ionization stage if it dissociates on the falling edge of the pulse; then, the laser intensity is not as high when it passes $R_e$.

The aim of our present investigation is to substantiate the above hypothesis. Two laser pulses of horizontal and vertical polarization are superposed with a time delay of less than the pulse duration, such that the ratio of the horizontal and vertical laser $E$-fields varies rapidly across the envelope of the combined pulse. Since the $\text{H}^+$ fragments are ejected preferentially along the laser $E$-field [5], this technique allows one to resolve dissociation events on a sub-pulse timescale.

The experimental arrangement is shown schematically in figure 2. A Ti:sapphire laser provides linearly polarized pulses of approximately 50 fs duration, 1 mJ in energy, at a wavelength of 790 nm and a repetition rate of 10 Hz. $\text{H}_2$ gas is introduced into the vacuum chamber through a fine tube pointing at the focal region. Ions are extracted from the interaction region by an electric field, pass through a field-free region and are detected with microchannel plates. Two groups of fragment peaks are observed, namely 'forward' ions with initial velocities towards the detector and 'backward' ions, whose initial direction is reversed by the extraction field. The time-of-flight (TOF) difference between corresponding forward and backward peaks is a direct measure of the release of ion kinetic energy in the dissociation or
Coulomb explosion process. The inset in figure 2 shows a typical ion TOF spectrum for H$_2$ [7].

The laser beam is fed through a Mach–Zehnder-like optical arrangement, so that two linearly polarized laser beams are focused in the vacuum chamber, one at an intensity of about $2 \times 10^{14}$ W cm$^{-2}$ and the other of about $4 \times 10^{14}$ W cm$^{-2}$. The overlap of the foci is optimized with the aid of a CCD camera. The delay line is adjustable to a precision of a few femtoseconds. With a half-wave plate in one of the arms, the polarization of one beam is made orthogonal to that of the other. The angular distributions of the fragments are measured by simultaneously rotating the polarizations of both laser beams with a half-wave plate located just in front of the vacuum chamber and taking ion TOF spectra at intervals of approximately 2°. Each TOF spectrum is an average over 100 laser shots.

'Momentum' maps of the energy and angular distributions of the forward H$^+$ ions, measured by rotating the polarization through 360°, are presented in figure 3 for six different delays, $\tau$. The radial scale, linear in momentum, shows the kinetic energy release (KER) in eV. The contour lines and the shades of grey show the signal strength of the ions. The grey scale is logarithmic so as to reveal the weaker features. At the side of each distribution, the laser pulses are drawn in perspective; the pulse drawn in front arrives first. The most energetic maxima, corresponding to kinetic energy releases of 4–9 eV, originate from the (1, 1) channel (see figure 2). The inner maxima at about 1 eV, are due to the (0, 1) channel and in particular to two-photon bond softening. We prefer not to use the term 'above-threshold dissociation', since the (0, 1) peak originates from vibrational levels that must absorb at least two photons in order to dissociate. The one-photon bond-softening peak ($\lambda\omega$, see figure 2), which is too
insignificant to be visible on the momentum maps, arises from more weakly bound levels. A further explanation of dissociation in intense laser fields can be found in a topical review on H$_2$ [8]).

As an aid to interpretation of the data, we first discuss those momentum maps for which the pulses are separated in time. For figures 3(a) and (b) the less intense pulses precede the stronger pulses by approximately 170 and 100 fs. Therefore, fragments are produced in the 'horizontal' direction, i.e. along the E-field of the weaker, leading pulse. However, the stronger pulse that arrives later produces more fragments in the vertical direction. Clearly, after the first pulse many stable molecules still remain in the focus. This is to be expected, since the
fragmentation of \( \text{H}_2 \) does not saturate until an intensity of about \( 3 \times 10^{14} \text{ W cm}^{-2} \) is reached [3, 7]. The angular widths of the maxima along the horizontal axis are as sharp as those along the vertical axis, showing that, for these delays, the second pulse does not affect the ejection angles of the fragments produced by the first pulse. Nevertheless, we will see later that the second pulse does have another effect on these fragments, i.e. post-dissociative ionization.

Even simpler is the momentum map of figure 3(f). In this situation the stronger pulse arrives first, depleting the focus of stable molecules. Hence very few fragments are ejected in the horizontal direction. The few that are stem from the periphery of the focus where the pump intensity remains below the saturation intensity and where the probe intensity rises above the appearance intensity [6].

For figure 3(d), the two pulses arrive simultaneously and combine to produce a single pulse of the same duration. The precise polarization of the combined pulse varies between linear and elliptical, depending on the relative phase between the two pulses. In general, the optical arrangement is not interferometrically stable and since the TOF spectra are averaged over 100 laser shots, coherence effects are relatively unimportant, although they sometimes show up as radial streaks on the momentum maps. In principle, however, the data of figure 3(d) are averaged over all possible polarizations for which the ratio between the vertical and horizontal components of the laser E-field \( E_x \) and \( E_z \) is the same, namely about \( 2^{1/2} \). Furthermore, since the pulse delay is zero, this ratio is constant along the whole pulse envelope. We can therefore use the angular distributions of the \((0, 1)\) and \((1, 1)\) channels obtained in figure 3(d) as standards, since they correspond specifically to this ratio between \( E_x \) and \( E_z \).

![Figure 4. For the short delays of \( \tau = -40 \) and 30 fs the individual pulses combine to give single peaked pulse with a rapidly varying ratio between \( E_x \) and \( E_z \). At \( t_{01} \) and \( t_{11} \) it is the same as the constant ratio for \( \tau = 0 \) fs.](image)

We now turn our attention to figures 3(c) and (e). The individual pulses, as well as the combined laser intensity, are plotted in figure 4. Clearly, for these short delays of \( \tau = -40 \) and 30 fs, the individual pulses combine to produce a single peaked pulse. For \( \tau = -40 \) fs, the polarization of the combined pulse varies from being purely horizontal at the beginning, to purely vertical at the end of the pulse. For \( \tau = 30 \) fs, the situation is reversed. In both cases, the ratio between \( E_x \) and \( E_z \) varies rapidly near the peak of the pulses.

From figure 3 we note that the \((1, 1)\) angular distributions for \( \tau = -40 \) and 0 fs are considerably wider than for \( \tau = 30 \) fs. The \((0, 1)\) features, on the other hand, show the opposite trend. For clarity, we present conventional polar plots of the area-integrated TOF peaks in figure 5. Let us compare the angular distributions for \( \tau = -40 \) and 30 fs with the standard distribution for \( \tau = 0 \) fs. Despite the jaggedness caused by coherence effects, it is evident that the \((1, 1)\) angular distributions for \( \tau = -40 \) and 0 fs are about equally wide,
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Figure 5. Polar plots of the area-integrated TOF peaks showing the angular distributions of the (0, 1) and (1, 1) channels. Despite the jaggedness caused by coherence effects, the similar widths of (a) and (b) and the relative sharpness of (c) strongly suggests that Coulomb explosion predominantly occurs on the rising edge of the pulse. The opposite trend shown in (d), (e) and (f), on the other hand, implies that the (0, 1) channel is produced on the falling edge of the pulse.

see figures 5(a) and (b). This suggests that, for \( \tau = -40 \) fs, Coulomb explosion occurs at times when the ratio between \( E_z \) and \( E_x \) is close to \( 2^{1/2} \). The exact moment when this ratio is achieved during the laser pulse is denoted by \( t_{11} \) in figure 4(a). The position of \( t_{11} \) at 15 fs before the peak of the pulse, indicates that Coulomb explosion does indeed occur on the rising edge of the laser pulse. The sharpness of the (1, 1) angular distribution for \( \tau = 30 \) fs, see figure 5(c), supports this conclusion since the ratio between \( E_z \) and \( E_x \) on the rising edge is high for this delay (see figure 4(b)).

In the case of the (0, 1) channel, it is the angular distribution for \( \tau = 30 \) fs which is about as equally wide as the standard one for \( \tau = 0 \) fs, see figures 5(e) and (f). This suggests that dissociation without enhanced ionization takes place on the falling edge of the pulse, since for \( \tau = 30 \) fs, the pertinent ratio of laser E-fields occurs at \( t_{01} \), see figure 4(b). Accordingly, the sharpness of the (0, 1) angular distribution of figure 5(d) is a result of the high ratio between \( E_z \) and \( E_x \) on the falling edge for \( \tau = -40 \) fs.

The above interpretation can be confirmed by data acquired for many more delays. In order to limit the amount of data, we concentrate on one angle. Whilst varying \( \tau \), we observe ions in the horizontal direction, i.e. along the E-field of the weaker pulse \( E_x \). This corresponds to either 0° or 180° in figure 3. For clarity, the ion spectra, measured at delay intervals of \( \sim 12 \) fs, are presented in figure 6 in two formats. The front of the surface plot of figure 6(a) corresponds to the top of figure 6(b).

The extent of the peak in the \( \text{H}_2^+ \) signal in figure 6 around \( \tau = 0 \) fs, a result of the nonlinearity of the ionization process, shows the range of pulse overlap. During the overlap, substantial variation in the \( \text{H}^+ \) TOF spectra is observed. Let us follow the path 'a', starting at the top of figure 6(b). At first the pulses are separated in time. The fragments with a KER of 1 eV stem from bond softening by the weaker pulse. For these positive delays, this is the second pulse and thus the ion signal is relatively low due to depletion of stable molecules by the first pulse. Following \( \alpha \) further down, the pulses start to overlap. The more intense, combined pulses produce more (0, 1) fragments, in particular for positive delays, since then the laser E-field on the falling edge of the pulses favours the direction of the detector axis.
Below the $\tau = 0$ fs line, on the other hand, the $(0, 1)$ fragments are ejected at relatively large angles and cannot be detected and hence the peak at 1 eV disappears. However, the angular acceptance for the slowest fragments is quite high and since the TOF is a measure of the initial momentum parallel to the detector axis [9], some of these fragments are still observed but with very small apparent KER, giving a maximum at 0 eV. Thus the positions of the maxima along $\alpha$ and $\beta$ confirm the association of the bond-softening peaks with the falling edge of the laser pulse.

Let us now follow path $\beta$ from the top of figure 6(b) downwards. At first we observe a small amount of Coulomb explosions induced by the second pulse. When the pulses start to overlap, the $(1, 1)$ peak grows and shifts towards higher KER as a result of the increased

**Figure 6.** Ion TOF spectra measured at delay intervals of $\sim 12$ fs in the (horizontal) direction of the $E$-field of the weaker pulse, corresponding to either 0° or 180° in figure 3. For clarity, the complex data are plotted in two formats. The positions of the maxima along paths $\alpha$ and $\beta$ confirm the interpretation of figure 5. The process observed along $\gamma$ is the initial creation of the $(0, 1)$ channel by the first pulse, followed by post-dissociative ionization by the second pulse.
peak laser intensity [3, 7]. The maximum peak height along $\beta$, however, is not reached at zero delay, because the laser $E$-field on the rising edge of the pulse is more inclined to eject ions towards the detector axis for negative pulse delays. Again, the position of the maximum along $\beta$ below the $\tau = 0$ fs line, confirms the interpretation of the momentum maps. Following $\beta$ after the maximum, we notice again a drop in KER, principally due to the decrease in peak laser intensity. Finally, the combined laser pulse separates into two individual pulses. The minimum KER on $\beta$ is achieved at a delay just before the pulses separate, since the longest pulse always yields the lowest Coulomb explosion energy [2].

Lastly, we follow $\gamma$ in figure 6(b), which starts when the individual pulses separate at $\tau \approx -100$ fs. In comparison to the (0, 1) peak produced by the horizontally polarized pulse alone, the $\gamma$ peak is twice as high. Furthermore, the KER of the $\gamma$ channel depends upon the delay between the well separated pulses. Clearly, the process observed here is the initial creation of the (0, 1) channel by the first pulse, followed by further ionization by the second, stronger pulse (post-dissociative ionization). Naturally, with respect to a pure (0, 1) channel, this leads to a doubling of the ion signal. The increase in KER is caused by Coulomb repulsion, which is of course greater for short delays. In effect, therefore, $\gamma$ is a branch of the (1, 1) channel and it is no coincidence that $\gamma$ appears as a bifurcation of $\beta$ when the pulses separate at $\tau \approx -100$ fs.

The present results substantiate the idea that the (0, 1) channel is relatively insignificant on account of the ease of enhanced ionization at $R_e$. Certain factors influence the probability of enhanced ionization. For instance, a longer pulse length or, more accurately, a longer fall time, should lower the signal of the bond-softening channel even further and indeed this has been observed experimentally [2]. On the other hand, if the nuclei can be made to approach $R_e$ more slowly, the (0, 1) channel should be enhanced. Indeed, when $H_2$ and $D_2$ are subjected to identical laser pulses, the relative number of (0, 1) fragments is significantly higher for the heavier isotope [3].

Finally, we can make a distinction between the faster and the slower parts of the dissociating nuclear wavepacket. Since the slower part of the wavepacket reaches $R_e$ later, its probability for enhanced ionization is not as high, because the laser intensity on the falling edge of the pulse has dropped further in the meantime. Thus, the (0, 1) kinetic energy distribution does not give a true representation of the original dissociating nuclear wavepacket, but favours the lower energies. In a high-resolution experiment, Rottke et al [10] recently found that the one- and two-photon bond-softening peaks originate, in particular, from the $v = 5$ and 2 vibrational levels of $H_2^+$, respectively. It is unlikely that field ionization of $H_2$ can populate the $v = 2$ and 5 levels, but not the $v = 3$ and 4 levels of $H_2^+$. We also reject the possibility that these levels remain stable, because a double-pulse experiment [6] shows that virtually all molecules in the focus are fragmented at high laser intensities. We note, however, that the $v = 3$ and 4 levels must absorb at least two photons in order to dissociate and thus constitute the fastest part of the two-photon dissociating wavepacket. Thus the relatively small contribution of the $v = 3$ and 4 levels to the (0, 1) peak is understandable, since these levels are less likely to survive enhanced ionization at $R_e$.

In summary, by superposing two laser pulses with a small time delay, we have produced single peaked pulses with a continuously varying ratio between the horizontal and vertical laser $E$-fields. Using the fact that the $H^+$ fragments are ejected preferentially along the laser $E$-field, we have demonstrated that Coulomb explosion of $H_2$ is primarily associated with the rising edge of the laser pulse. On the other hand, the ion ejection angles of the bond-softening channel yield direct evidence that the $H + H^+ + e^-$ channel is primarily produced on the falling edge of the pulse, in agreement with the notion that only then can enhanced ionization at the critical internuclear separation be avoided. Finally, we have given a consistent explanation
for the surprisingly small energy spread of the bond-softened peaks, as observed in a recent high-resolution study.

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References

Appendix 7.6
Short Pulse Laser Interaction with Positive Ions

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Abstract
The viability of using beams of molecular ions as a target for strong field fragmentation studies using intense ultra-short laser pulses is demonstrated. In this way the production mechanism for multiply charged ions in strong fields may be elucidated.

1. Introduction
In recent years, the study of short pulse laser interactions with neutral atoms and molecules has led to the discovery of new effects in strong field physics. These include above threshold ionization and dissociation, bond softening and Coulomb explosions [1]. Most recently atomic clusters have been used as targets, with resulting observations of coherent X-rays [2], and of high energy ions [3]. In this paper we describe a new experimental arrangement, designed to carry out such experiments with ionized targets.

To date experimental studies designed to observe fragmentation of molecular ions by short laser pulses have used neutral molecule targets and relied on the assumption that the ionization of the molecule and the dissociation of the molecular ion, occurring in the same laser pulse, are sequential processes. There is evidence to support that this assertion is generally true for pulse durations greater than about 1 ps. However when the pulse durations are significantly less than a ps, such that they approach the vibrational period of the molecules, a sequential description of the processes may well break down, and a simultaneous treatment may be more appropriate [4]. Moreover, the use of neutral targets has the distinct disadvantage that as the laser intensity is varied the molecular ion will be produced in differing states of internal energy.

2. Experimental arrangement
A schematic diagram of the experimental arrangement, as used in the preliminary study on H₂⁺ ions is shown in Fig. 1. Molecular ion beams can be extracted from suitable sources, focussed by a five-element cylindrical lens system, and momentum selected for purity in a 30° bending magnet. Further focussing by a three-element aperture lens system and path correction by electrostatic deflection plates occur in a differentially pumped chamber. The deflectors may also be used for ion beam modulation. The molecular ion beam then enters the interaction and analysis chamber which is maintained at a base pressure of about 5 x 10⁻¹⁰ mbar.

At the point of interaction the molecular ion beam is intersected by a reflection focussed, pulsed laser beam. A Ti:Sapphire oscillator, pumped by an argon ion laser, produces femtosecond pulses which are subsequently amplified using the chirped amplification process to give 2 mJ pulses at 10 Hz. The laser, housed at the Rutherford Appleton Laboratory, currently delivers radiation pulses of 50 fs duration at a wavelength of 790 nm. These pulses are monitored using a single shot autocorrelator. When focussed to a spot size of 4 µm diameter, laser intensities of approximately 10¹⁰ W cm⁻² can be produced. However due to the low target densities available in a typical low energy ion beam (approximately 10¹⁰ cm⁻²), it is more appropriate to focus to a larger spot size with a correspondingly longer confocal length. In the study of H₂⁺ ions a spot size of 0.1 mm, with confocal length of approximately 15 mm was used. This gave a maximum pulse intensity at the point of interaction of 7 x 10¹¹ W cm⁻².

Following laser dissociation of the H₂⁺ ion the fragments H and H⁺, which retain the initial ion velocity, are subjected to electrostatic deflection which separates the primary 2500 eV H₂⁺ ion beam from the product 1250 eV H⁺ beam. The H₂⁺ ions are monitored using a Faraday collector while the H⁺ ions and the H neutrals are detected using channel electron multipliers. In addition to the spatial separation of the ions a time of flight analysis was also performed on the fragmenting products. The laser pulse provided the start pulse for the timing electronics with the ions timed over the 27 cm flight path between the point of interaction and the channel electron multiplier detectors.

Fig. 1. Schematic diagram of the laser-ion apparatus.

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3. Results

Results obtained for the fragmentation of $H_2^+$ ions by 790 nm, 50 fs laser pulses are shown in Fig. 2. Protons may be produced either through dissociation:

$$H_2^+(1\sigma_g, v) + n\hbar\omega \rightarrow H^+ + H(n, l)$$  \hspace{1cm} (1)

or through ionization, via a Coulomb explosion:

$$H_2^+(1\sigma_g, v) + n\hbar\omega \rightarrow H^+ + H^+ + e.$$  \hspace{1cm} (2)

With the laser polarization fixed along the ion beam direction, Coulomb explosions would be witnessed by two distinct peaks in the proton time-of-flight spectrum. This is due to protons being ejected preferentially in the forward and backward directions with peak energies of about 3 eV in the centre-of-mass frame of reference [5]. Kinematic shifts would result in such protons having laboratory energies of approximately 1250 ± 120 eV. Such double peaks were not observed in the current study, with only a single strong peak at the central energy of 1250 eV present in the spectra. Hence the proton yield plotted in figure 2 relates entirely to the dissociation channel (eqn. (1)). With a maximum laser intensity of $7 \times 10^{13}$ W cm$^{-2}$, this is in qualitative agreement with a theoretical prediction that the Coulomb explosion channel in $H_2^+$ has a threshold of $8 \times 10^{13}$ W cm$^{-2}$ [6]. This prediction is based on a simulation of the appearance intensity curves for Coulomb explosions in $H_2$ [5], where transition rates are described by power laws of the form, $T_\ell = a\ell^\eta$, and the semi-empirical parameters $a$ and $\eta$ are found through fitting to experimental data. A similar calculation for the dissociation channel (eqn. (1)) in $H_2^+$ puts the threshold at about $2 \times 10^{13}$ W cm$^{-2}$, which is higher than that observed in the present measurement.

4. Conclusion

The present measurement of the dissociation of $H_2^+$ as a function of laser intensity, demonstrates the viability of using molecular ion beams as targets for studies involving intense ultra-short laser pulses. Current upgrades to the laser system will permit extension to the regime where Coulomb explosions may be observed. In order to address the issue of fragmentation dynamics in strong fields, and as pulse durations approach 1 fs, further studies will focus on more complex molecular ions, with products analysed for both charge state and fragmentation energy. Experimentally this will require the primary ion beams to be energy selected, coupled with a more sophisticated analysis and detection system for the fragmentation product ions. In this way the production mechanism for multiply charged ions in strong fields may be elucidated.

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References

Appendix 7.7

Laser-induced Coulomb explosion, geometry modification and reorientation of carbon dioxide

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Abstract. The Coulomb explosion of carbon dioxide in a 55 fs laser pulse of intensity 1.5–3 × 10¹⁶ W cm⁻² has been studied using a variety of techniques based on time-of-flight mass spectroscopy. Covariance mapping has been used to identify Coulomb explosion channels and to measure the associated kinetic energy release. By comparing time-of-flight spectra taken with linearly and circularly polarized light, a clear signature of laser-induced reorientation is found, which is strongest for the lowest Coulombic channel. Ion-momentum imaging coupled with Monte Carlo simulation shows that the zero-point bend-angle distribution is better preserved than for longer laser pulses. However, some residue of the sequential processes dominant in much longer pulses is found.

1. Introduction

The development of tabletop femtosecond lasers has allowed dramatic progress in the understanding of the behaviour of small molecules in intense electric fields. The alignment and ionization of diatomic molecules in high-intensity plane-polarized laser fields is now reasonably well understood in terms of enhanced ionization [1–3]. A number of studies of triatomics [4–14] have been carried out over the last ten years with increasing pulse energies and decreasing pulse duration, including two attempts to quantitatively describe the bend angle as well as bond length [6,12]. These experiments have both shown that modifications to the neutral bend-angle distributions occur during multiple ionization and Coulomb explosion. In the case of H₂O in a 55 fs laser pulse [12], the molecule was found to straighten substantially, and in the case of carbon dioxide [6] in a 150 fs pulse, an enhanced distribution of bend angles was observed. By using a combination of covariance mapping [8] and ion-momentum imaging incorporating finite-angle correction [12], we can study the geometry of carbon dioxide in a 55 fs laser pulse of intensity 3 × 10¹⁶ W cm⁻². These current techniques have also produced information about the reorientation and dissociation dynamics. The experimental system used in this work is identical to that used in Sanderson et al [12,13]. Moreover, a full description of the ion-momentum imaging technique is given here, including the Monte Carlo technique used to simulate the Coulomb explosion process.

Previous investigations of the Coulomb explosion of carbon dioxide have noted the narrow angular distribution of the energetic fragment ions [6,13]; this has been attributed to laser-induced molecular reorientation. However, no conclusive experimental evidence has been put
forward that differentiates this phenomenon from preferential ionization of initially aligned molecules. We hope to make this distinction by comparing the Coulomb explosion of carbon dioxide in linearly and circularly polarized laser pulses, for which the average laser electric field in the direction of the detector has been made equal [15].

2. Experimental

A schematic diagram of the laser system used in this work is presented in figure 1(a). An argon-ion laser pumps a Ti:sapphire oscillator, producing around 9 nJ in 50 fs at $\lambda = 790$ nm. An all-reflective stretcher, comprised of a 1500 lines/mm grating and a concave mirror, is used to increase the pulse duration to 180 ps. The stretched pulses are then amplified in a multi-pass confocal amplifier containing a Ti:sapphire crystal, pumped with 67 mJ from a Nd:YAG laser. The stretched pulses pass through the crystal five times and are controlled by four spherical mirrors, each with a radius of curvature of 2000 mm. The preamplified pulse train is then removed from the amplifier and passed through a pulse picker. This reduces the repetition rate from 82 MHz to 10 Hz. The selected pulse is then reinjected into the amplifier, where the pulse energy is raised to 4 mJ. A pair of 1500 lines/mm gratings in parallel arrangement then compress the pulse back to 50 fs. The output pulse duration is monitored with a single-shot autocorrelator. Following the compressor, beam-steering mirrors control the beam path into the apparatus. A half-wave plate mounted in a rotation stage controls the polarization direction and a quarter-wave plate can be inserted into the beam path after the half-wave plate to produce circular polarization. Following optical losses, 900 $\mu$J per pulse enters the vacuum chamber through a fused-silica window.

Transmission of the 50 fs pulse through the window causes a temporal dispersion of 10%, giving a final pulse length in vacuum of 55 fs. The laser pulse is then focused with an on-axis $f/5$ spherical mirror. Pulse-to-pulse energy fluctuations are detected by a photodiode (PD), monitoring the reflection from the entrance window. This signal is fed into a single-channel analyser (SCA), which produces the trigger for a digital storage oscilloscope (DSO) provided the PD pulse is within $\pm 10\%$ of the required level.
Laser-induced Coulomb explosion in carbon dioxide

Figure 1(b) illustrates a schematic of the time-of-flight mass spectrometer (TOFMS), which employs the Wiley–McLaren [16] geometry. The laser focus is situated at the centre of the source region of the spectrometer. Gas is introduced into the spectrometer through a hypodermic needle 1 cm from the laser focus, typically raising the pressure from $1 \times 10^{-9}$ to $1 \times 10^{-7}$ Torr. Ions are extracted from the source region by the applied electric field $E_1$, and accelerated by $E_2$. The ions then drift through a field-free region at the end of which is a removable aperture, 3 mm in diameter. Ions transmitted by the aperture are accelerated through a grid onto a pair of channel plates, 25 mm in diameter, mounted in a chevron formation. The channel plate signal is fed directly into a Tektronix TDS 744A DSO, interfaced to a laboratory PC via a GPIB link.

2.1. Determination of the focused laser intensity

Two approaches were used to determine the focused laser intensity. Firstly, calculations were made of the radius, $\omega_0$, of the focal spot, using the laser wavelength (790 nm), the focal length of the spherical mirror (5 cm) and the beam diameter (1 cm). The beam is 1.5-times diffraction limited and, assuming a Gaussian profile, $\omega_0 = 3.75 \mu m$. The intensity was then calculated from the pulse characteristics (900 $\mu$J in 55 fs) and was found to be $3 \times 10^{15}$ W cm$^{-2}$ within an Airy disc containing 86% of the pulse energy. Secondly, using an experimental approach, xenon and argon were introduced independently into the spectrometer, and their stages of ionization determined. The highest stages of ionization observed were Xe$^{8+}$ and Ar$^{7+}$, for which appearance intensities of $8 \times 10^{15}$ and $3 \times 10^{16}$ W cm$^{-2}$, respectively, were determined by Augst et al [17], which is consistent with the calculated laser intensity.

2.2. Identification of the Coulomb explosion channels and measurement of kinetic energy release

We have previously used a simple one-dimensional TOF technique in the study of alignment and bending in the Coulomb explosion of carbon dioxide from the ground state [13] and from vibrationally excited states [14]. 'Channel-resolved' experiments employing covariance mapping or coincidence detection have allowed identification of the explosion channels and measurement of the kinetic energy release (KER). Cornaggia [6] and Hering and Cornaggia [10] employed double covariance, Cornaggia et al [7] and Frasinski et al [9] used triple covariance, and Sanderson et al [18] used triple coincidence in conjunction with a position- and time-sensitive detector. In these experiments, laser pulses of 80 fs [10], 150 fs [6, 7] and 200 fs [9] and highly charged ion (HCI) impact [18] were used to multiply-ionize the molecule. A comparison with HCI impact seems appropriate, as in this process field ionization is also the dominant ionization mechanism. In this section, we present the Coulomb explosion channels observed, and the total KER associated with each channel determined by two-dimensional covariance mapping.

In this experiment, the laser polarization was set parallel to the axis of the TOFMS and the aperture was removed to ensure near-unity collection efficiency. The number of laser pulses and hence number of individual TOF spectra recorded was of the order of $10^5$. The experiment was performed at a pressure of $3 \times 10^{-3}$ Torr; this pressure was necessary to keep the ion signal low at around 3–4 dissociations per laser shot.

At the intensities present in the laser focus, carbon dioxide may be ionized three or more times (up to CO$_2^+$ under present conditions), with explosion into three atomic ions being the dominant process. By applying conservation of momentum to the explosion, i.e. measuring the momenta of pairs of correlated ions, fragmentation channels may be identified. Figure 2 shows
Figure 2. Covariance map of the fragment ions from the Coulomb explosion of carbon dioxide, recorded with $10^6$ laser pulses. The pulse length is 55 fs, generating an intensity of $3 \times 10^{14} \text{W cm}^{-2}$ at 790 nm. The laser polarization is parallel to the axis of the TOFMS. The detected ions are labelled on the y-axis. The subscripts $f$, $m$ and $b$ correspond to ‘forward’, ‘middle’ and ‘backward’ ions. Note the correlation between the $\text{O}_2^+$ and $\text{CO}^+$ ions is overlapped with the autocorrelation line. The enlarged region contains the following correlations: (a) $\text{O}^+ + \text{O}^+$, (b) $\text{O}^+ + \text{C}^+$, (c) $\text{O}^+ + \text{O}^{2+}$ and (d) $\text{O}^+ + \text{C}^{2+}$.

A covariance map, in which the ions detected are labelled on the y-axis. The subscripts $f$, $m$ and $b$ correspond to the ‘forward’, ‘middle’ and ‘backward’ ions. The forward ions initially travel in the direction of the detector and the backward ions away from it, but are turned around by the applied field $E_1$. Middle ions are thermal or from low-energy dissociation. This notation also applies to figures 3 and 6. The identification procedure is demonstrated in the enlarged section of the map, where the following correlations are present: (a) $\text{O}^+ + \text{O}^+$, (b) $\text{O}^+ + \text{C}^+$, (c) $\text{O}^+ + \text{O}^{2+}$ and (d) $\text{O}^+ + \text{C}^{2+}$. The dashed line corresponds to the peak of correlation (a), which passes through the peak of correlation (b); correlations (c) and (d) are observed to peak at higher momenta. Correlations (a) and (b) therefore constitute a Coulomb explosion channel, as momentum is conserved in the oxygen ions; this is the $\text{CO}_2^+ \rightarrow \text{O}^+ + \text{C}^+$ channel. All of the explosion channels identified in this manner are presented in table 1 along with the total KER and the Coulombic kinetic energy (CKE) from the ground state equilibrium position. The results of [7,9,10,18] are also included. The notation $(M, N, P)$ in table 1 corresponds to the dissociation channel $\text{CO}_2^+ \rightarrow \text{O}^+ + \text{C}^+$.

Comparing the ratio $k = \text{KER}/\text{CKE}$ from this work with those from [7,9,10,18], the same general trend is observed: $k$ decreases slightly with increasing pulse length. In the HCI experiment [18], roughly the same range of channels was observed [19] although the KER has only been calculated for those channels reported. The values of $k$ observed in the present and previous laser experiments show some scatter, but an average taken across all channels shows a small systematic increase in $k$ with decreasing pulse length. This observation is in agreement with the behaviour of diatomic molecules field ionized by 400 and 50 fs laser pulses [1]. The relatively small magnitude of the increase is due to the importance of the
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Table 1. Total KER for the explosion channels identified by two-dimensional covariance mapping.

The experimental values are then compared to the CKE generated by explosion from the ground state equilibrium position. The ratio of these two values \( k \) is then compared with those measured in [7,9,10,18]. \( k_{\text{exp}} \) is the mean \( k \) over all observed channels at each pulse duration.

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<td>((2,1,3))</td>
<td>70</td>
<td>124</td>
<td>0.51</td>
<td>0.50</td>
<td>0.56</td>
<td>0.55</td>
<td>1.22</td>
</tr>
<tr>
<td>((2,2,1))</td>
<td>90</td>
<td>161</td>
<td>0.57</td>
<td>0.57</td>
<td>0.56</td>
<td>0.55</td>
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<tr>
<td>((2,2,2))</td>
<td></td>
<td>174</td>
<td>0.50</td>
<td></td>
<td>0.52</td>
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</tr>
<tr>
<td>((2,2,3))</td>
<td>100</td>
<td>223</td>
<td>0.45</td>
<td>0.45</td>
<td>0.49</td>
<td></td>
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<tr>
<td>((3,3,3))</td>
<td>116</td>
<td>279</td>
<td>0.39</td>
<td>0.47</td>
<td>0.42</td>
<td>0.51</td>
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</tr>
</tbody>
</table>

\[ k = \text{KER}/\text{CKE} \]

\[ k_{\text{exp}} = 0.5 \]

critical distance, \( r_c \) [1–3]. The results from the HCI experiment are interesting as they show \( k \geq 1 \), where explosion has occurred from around the ground state equilibrium position. The HCI impact can be viewed as a unidirectional electric field pulse in which the HCI–molecule interaction time is around 1 fs, causing field ionization. Although interactions between the HCI and molecule such as momentum transfer complicate the situation, this observation indicates that the dominance of the critical distance in field ionization could be overcome with a laser pulse of a few femtosecond in duration. In this case, Coulomb explosion will occur from the ground state equilibrium position. The channel information and KER will be utilized in sections 2.4 and 3, where an ion-momentum imaging technique is used to study the geometry of the exploding molecule.

2.3. Experimental investigation of molecular reorientation

There has been considerable contemporary debate concerning molecular reorientation within linear polarized laser pulses. The term ‘reorientation’ implies changing the initial random distribution of the molecules in the laser focus such that the inter-nuclear axes of the molecules rotate towards the polarization direction. A number of experimental studies have investigated this process in a range of diatomic molecules [11,15,20,21] ranging from \( \text{H}_2 \) to \( \text{I}_2 \). These studies showed that, whilst the massive \( \text{I}_2 \) molecule is not reorientated, lighter molecules from \( \text{Cl}_2 \) to \( \text{H}_2 \) were substantially influenced by the laser electric field. Molecular reorientation has been used to explain results in similar experiments in triatomics. In Sanderson et al [13], the narrowing of a fitted distribution \( (A \cos^2 \theta) \) with explosion channel was taken to infer reorientation in carbon dioxide, where \( \theta \) is the angle between the laser polarization and the axis of the TOFMS, and \( A \) is an arbitrary scaling parameter. We reported that \( n \) increased from \( n = 12 \) for the \((1,1,1)\) channel to \( n = 16 \) for the \((2,3,2)\) channel. However, the distinction has not been made experimentally between reorientation ionization and preferential ionization of initially aligned molecules. In order to rectify this, we have investigated this phenomenon by comparing TOF spectra recorded with linear and circular polarization [15].

Firstly, a TOF spectrum was recorded with linear polarization; at a pulse energy of 450 \( \mu \text{J} \).
the polarization was set parallel to the axis of the TOFMS. The aperture was present in the spectrometer (see figure 1(b)), thus only fragments from those molecules which exploded along the TOF axis within the angular acceptance \( \varphi_{\text{ACC}} \) were observed, where \( \varphi_{\text{ACC}} \) is small for energetic fragments. The pulse energy was then doubled to 900 \( \mu \text{J} \), and a quarter-wave plate inserted into the beam path to produce circular polarization; this is illustrated in figure 1. The circularity of the polarization was tested by placing a linear polarizer after the quarter-wave plate, and measuring the laser pulse energy as a function of polarizer angle. The pulse energy was found to be constant to within 5\%, indicating good circularity. A second TOF spectrum was then recorded with circular polarization but with double the energy of the linearly polarized beam, such that the average electric field (\( e \)) in the direction of the detector was the same in both cases.

To predict what differences might be observed in the TOF spectra, it is necessary to consider the ionization process for both types of polarization. We assume that the final ionization stage reached by a carbon dioxide molecule is determined by the maximum magnitude of the laser \( e \)-field along the \( \text{O-O} \) axis [1]. In the case of circularly polarized light, ionization is governed only by the location of the molecule within the laser focus, as the electric field strength is the same in all directions. The molecules effectively ‘sample’ the maximum laser intensity. With linearly polarized light (if reorientation is absent), ionization is dependent not only on the location of the molecule within the focus but also the initial orientation of the molecule with respect to the laser polarization direction. Throughout the focus, molecules that are well aligned with the laser polarization experience the strongest \( e \)-field along their \( \text{O-O} \) axis and are ‘preferentially’ ionized. This leads to the characteristic distribution of energetic fragment ions along the polarization direction; hence when the polarization direction is parallel to the TOFMS axis, these energetic fragments will be detected.

In the case of circularly polarized light, the direction of the energetic ions is isotropic, but because \( \varphi_{\text{ACC}} \) is small (\( \varphi_{\text{ACC}} \approx 10^{\circ} \)), only those ions emitted in the direction of the detector are collected. The number of molecules that are coincidently aligned with the spectrometer axis is identical in both cases and the laser electric field has been made the same in both cases. Hence, if molecular reorientation is absent, and only preferential ionization occurs, the signal for a given fragment ion will be the same for both polarizations. Conversely, if there is more ion signal with linear polarization, it indicates that reorientation has occurred.

Presented in figure 3 are the TOF spectra of carbon dioxide recorded with linear and circular polarization. The average ion signal strength of the \( \text{CO}_2 \) parent ion is comparable in both cases. However, for all other stages of ionization, the spectrum recorded with linear polarization exhibits a significant increase in ion signal. The straightforward conclusion from figure 3 is that carbon dioxide is substantially reorientated during the interaction with the laser pulse. However, we would like to derive more detailed information for each ion and we can do this by integrating the signal under each peak for the linear \( I \) (lin) and circular \( I \) (circ) cases and taking the ratio \( R_{\text{ROT}} = I \) (lin) : \( I \) (circ).

The variation of \( R_{\text{ROT}} \) with ion species and the predominant channel of origin is presented in figure 4. The first distinction to be made is between the high-momentum and low-momentum ions, on the upper and lower curves, respectively. As discussed above, the experimental technique is designed to work with high-momentum ions but we can look at the variation of \( R_{\text{ROT}} \) for the low-momentum ions provided we consider the much greater acceptance angle \( \varphi_{\text{ACC}} \) for these ions. The effect of this increase in \( \varphi_{\text{ACC}} \) is to boost \( I \) (circ) and, therefore, to artificially lower \( R_{\text{ROT}} \) — hence the two distinct curves of figure 4. For example, the \( \text{CO}_2^+ \) ion has no momentum from dissociative recoil, only from thermal motion, and so \( \varphi_{\text{ACC}} = 90^{\circ} \) (figure 5); this means that all ions are detected. For \( \text{CO}_2^+ \), \( R_{\text{ROT}} \approx 1 \) and this indicates that even for this low-intensity process, reorientation occurs, as without reorientation there would
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Circular Polarisation
Linear Polarisation

Figure 3. TOF spectra of carbon dioxide recorded with 55 fs laser pulses. The solid plot indicates the spectrum taken with linear polarization with a pulse energy of 450 µJ. The laser polarization direction is parallel to the axis of the spectrometer, as indicated in figure 1. The dashed plot indicates the spectrum taken with circular polarization, with a pulse energy of 900 µJ.

Figure 4. Variation of the reorientation coefficient \( R_{\text{ROT}} \) with ion species, indicating the predominant channel from which they emanate. The ions fall into two groups: high-momentum ions (solid curve, top) which come from Coulombic channels and low-momentum ions (bottom) from Coulombic channels (dashed curve), dissociative ionization (short-dashed curve) and singly and doubly ionized parent molecule (dotted curve).
be substantially more CO$_2^+$ signal with the circular polarization light, because more energy is deposited in the focus. For CO$_2^{2+}$, $R_{\text{ROT}} > 1$, indicating that the amount of reorientation has increased with ionization channel. Examining the variation of $R_{\text{ROT}}$ with channel we see the same pattern for both low- and high-momentum ions: $R_{\text{ROT}}$ increases with channel up to the (1, 1, 1) channel and then decreases for the higher channels. In order to determine that this drop in $R_{\text{ROT}}$ is not an instrumental effect due to an increase in $\varphi_{\text{ACC}}$, particularly for the high-momentum oxygen fragments, the value of $\varphi_{\text{ACC}}$ for O$, O^2+$ and O$^3+$ has been calculated at the average measured momentum of each ion and the results are shown in the inset of figure 5. It appears that there is actually a small decrease in $\varphi_{\text{ACC}}$ with increasing stage of ionization. The effect of this is to cause a slight increase in $R_{\text{ROT}}$ with ionization stage. It therefore appears that the observed decrease is physical and not instrumental in origin. The dependence of $R_{\text{ROT}}$ on ion species indicates that most reorientation is experienced by molecules that explode into the (1, 1, 1) channel (i.e. the O$^+$ and C$^+$ ions); the importance of this process decreases for the higher-order channels which involve the O$^{2+}$, O$^{3+}$, C$^{2+}$ and C$^{3+}$ ions. If we assume that the final ionization step takes place at or near the peak of the pulse, which is reasonable [16], then the ions that experience maximum reorientation are, at most, doubly ionized. These molecules then go on to explode into the (1, 1, 1) channel on the removal of the third electron. The amount of reorientation produced therefore depends on the point within the laser pulse that the third electron is removed, hence, the earlier the third electron is removed, the less reorientation occurs. As a consequence of this process, the high-order channels experience less reorientation as the third electron is removed very early in the pulse. The fact that the angular distributions sharpen for higher channels [13] must indeed be the effect of preferential ionization, as discussed earlier.

The strength of the reorientation process is dependent on the $e$-field experienced by the molecule (as before, dependent on location within the focus and initial orientation), its polarizability and moment of inertia. The moment of inertia of the molecule is similar over the
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range of channels as Coulomb explosion occurs at around double the ground state equilibrium position. Furthermore, the e-field strength necessary to produce the higher channels increases accordingly [22]. It therefore appears that a drop in the polarizability of the molecule could be responsible for the lower reorientation of the highest channels. The CO$_2^+$ and more highly charged ions are exploding coulombically, whereas the CO$_2^{3+}$ ions are dissociating more gently. It may be this difference which effects the electrons freedom of movement; in addition the effect of laser-induced electron localization [2] may be important.

2.4. Determination of molecular geometry using ion-momentum imaging

As discussed in section 2.3, we have previously measured the angular distributions of the carbon and oxygen ions emitted from the Coulomb explosion of carbon dioxide [13] in order to investigate the effects of laser-induced reorientation and geometry modification. While the oxygen ions were emitted along the laser polarization, the carbon ions were emitted perpendicular to the polarization direction. This distinct orthogonality of the ion trajectories could only result from Coulomb explosion of a bent molecule. A similar deduction was made by Cornaggia [6] using the two-dimensional covariance mapping technique, in which the best agreement between the data and a Monte Carlo simulation of the molecular structure was found with a wide bend-angle distribution peaked at $\theta = 180^\circ$. By developing the ion-momentum imaging technique of Hishikawa et al [11], we have also been able to obtain structural information about the H$_2$O molecule [12], which was found to straighten substantially during the ionization process. In the current work, we apply this technique to carbon dioxide to measure the O-C bond length ($r$) and O-C-O bend angle ($\theta$), along with measuring the angular distributions of the carbon and oxygen ions with respect to the laser polarization direction.

The TOFMS was operated as in section 2.3, with the aperture present but using only linearly polarized light. A series of TOF spectra were recorded as a function of angle $\beta$ between the laser polarization and the axis of the spectrometer. This was performed by slowly rotating the half-wave plate and recording spectra at two-degree intervals. The DSO averaged the ion signal over 100 laser shots, then passed the spectrum to the PC. Following a 360° rotation of the polarization, the spectra were recalled in bulk to form a TOF matrix. Figure 6(a) shows a three-dimensional TOF matrix for carbon dioxide. The x-axis is TOF in seconds, the y-axis is $\beta$ in degrees and the z-axis is the ion signal intensity on a colour scale. To aid ion identification, a horizontal section through the TOF matrix at $\beta = 0^\circ$ is shown in figure 6(b). A number of qualitative observations may be made from the TOF matrix. The very low momentum ions CO$_2^+$, CO$_2^+$, CO$_2^+$ and O$_2^+$ appear as uniform vertical stripes, independent of $\beta$. These ions have little momentum as they originate from the lowest channels such as pure ionization or dissociative ionization, and as such the maximum signal for these ions occurs at flight times corresponding to zero initial momentum, referred to as $t(p_0)$. The values of $t(p_0)$ are known for all the observed ions as $t(p_0) \propto (m/q)^2$ where $m/q$ is the mass-to-charge ratio. All the atomic ions exhibit non-uniform behaviour: for example, the C$_{21}^+$ ions appear as forward–backward islands situated either side of $t(p_0)$ at values of $\beta$ around 0° and 180°, and the C$_{31}^+$ ion appears as a stripe of varying width which is widest at 90° and narrowest at around 0° and 180°. The C$_{21}^+$ ion and the backward O$_{31}^+$ ion overlap producing a feature, which combines aspects of both ions, broadening at 0°, 90° and 180°. The implications of these distributions are more easily visualized from ion-momentum images (IMIs) where the signal intensity of an ion is plotted on a polar map. The radial coordinate represents momentum derived from flight time by the formula $p = K(q(\Delta tE_1))$, where $p$ is momentum in amu ms$^{-1}$, $\Delta t = t(p_0) - t$ in ns, $q$ is the ion charge in au, $E_1$ is the extraction field in V cm$^{-1}$, and $K = 9.8$. The angular coordinate $\beta$ represents the angle between the ion trajectory and the laser polarization.
Figure 6. (a) TOF matrix of carbon dioxide recorded by rotating the laser polarization through 360° in 2° steps. The angle $\beta$ indicates the angle between the laser polarization and the axis of the TOFMS. (b) TOF spectrum at $\beta = 0$, to allow ion identification.
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direction. IMI plots are presented for all atomic ions in figure 7 and it is quite clear from
them that the oxygen and carbon ions exhibit markedly different behaviour. Apart from O+
which has some signal at zero momentum in figure 7(a), the oxygen ion signals all appear as
double islands, parallel to the laser polarization direction, and with non-zero momentum. This
indicates that the ions are emitted with high momentum along the laser polarization direction.
However, the carbon ion signals appear as single elliptical islands, centred at zero momentum,
with their major axis perpendicular to \( \epsilon \), indicating that the ions are emitted with low or zero
momentum but preferentially perpendicular to the laser polarization direction.

By considering the range of momenta in the IMI plots over all oxygen ions, we can derive
information about the dissociation channels that occur. This is possible because the oxygen
fragments take away the majority of the momentum, as the carbon atom is in the middle of the
molecule. As an example, the highest momentum with which O+ ions are detected (figure 7(d))
is \( 300 \times 10^3 \text{amu ms}^{-1} \); this is near to the middle of the momentum range of the O2+ signal
in figure 7(e). We can therefore deduce that explosion channels involving O+ and O2+ such as
(1, 1, 2) or (1, 2, 2) are occurring. However, there is no overlap in momentum between the
O+ and O2+ ions, so we deduce that no channels involving these ions are occurring. Both of
these conclusions agree with the information gained from covariance mapping in section 2.2.

By comparing fragment-ion momenta we can gain an insight into the origin of the two
rings present on the O+ IMI plot at \( p = 100 \times 10^3 \text{amu ms}^{-1} \) and \( p = 280 \times 10^3 \text{amu ms}^{-1} \)
in figure 7(e). These rings are not present in either the O2+ or O3+ plots, nor are they present
in the CO+ IMI, which is not shown. Furthermore, they cannot originate from a symmetric
O+ + O+ channel (for example, the (1, 1, 1) channel) as the O+ ion momentum will lie in the
momentum range between the two rings, as derived from the covariance mapping experiment.
This implies that these signals are not due to O+ from any explosion or dissociation channel.
Further analysis has shown that the positions of these features correspond to values of \( t(t_0) \) for
the multiply charged ions CO2+ (inner ring) and CO3+ (outer ring) on the TOF matrix. They
only appear as rings of finite momentum because the map is calculated using the value of \( t(t_0) \)
for O+. The presence of the residual CO2+ signal is not surprising, as recent experiments have
shown that femtosecond laser pulses may produce metastable triply charged parent ions (Sakai
et al [23]). The presence of CO3+ is more puzzling, as it has no recoil momentum, as the ion
signal is at a maximum at \( p_0 \). This ion must therefore be produced either in an asymmetric
process \( \text{CO2}^+ \rightarrow \text{CO2}^+ + \text{O} \), or as the result of the sequential process \( \text{CO2}^+ \rightarrow \text{CO}^+ + \text{O} \),
followed by \( \text{CO}^+ \rightarrow \text{CO2}^+ \). The sequential process is more plausible, as no evidence has
been found of any other channels in which the dissociating partners differ in charge by more
than one unit, as seen in table 1. The presence of CO2+ probably explains the signal observed
in our previous work, which was carried out under much poorer signal conditions [13]. In
that work, the low-energy O+ signal exhibited a second maximum perpendicular to the laser
polarization direction and was tentatively assigned to molecules reorientated in this direction
and drastically bent. However, the superior resolution in both angle and momentum in the
present experiment now allows us to rule out this conclusion.

The IMI plots presented in figure 7 can be interpreted in terms of the geometry of the
exploding carbon dioxide molecule. If the molecule is linear and the two O-C bonds break
simultaneously, the carbon ions will receive no initial momentum from Coulomb explosion
except from asymmetric channels, which will result in carbon ions being emitted along the
O-C-O axis. However, if the molecule has a bent geometry, the carbon ion will receive
significant momentum perpendicular to the O-O axis. In the case of C+, C2+ and C3+ ions, the
peak in the ion signal is at zero momentum, but extends in the direction perpendicular to the
oxygen trajectories. An uncritical interpretation of figure 7 leads to the conclusion that there
is a distribution of bend angles peaked at \( \theta = 180^\circ \).
Figure 7. IMI plots produced from the data presented in figure 6. The arrow indicates the direction of the laser polarization. The signal at high momentum along the laser polarization in (a) and (b) is due to the overlap of adjacent ions, as in the 'ring' around the circumference of (d).
We would like to draw quantitative information about the molecular geometry from the IMI plots. This is possible by simulating the Coulomb explosion of molecules with model distributions of the O–C bond length and O–C–O bend angle. However, so far no account has been made for the considerable variation of collection efficiency with ion momentum and species: this problem must be addressed. By reducing the angular acceptance $\varphi_{\text{ACC}}$ of the detector, there is an enhancement in ion signal strength for low momentum ions with respect to high momentum ions as low momentum ions are preferentially detected (as discussed earlier). Quantitative correction for this instrumental effect is possible and the true structure of the exploding molecule will only be resolved after this correction has been carried out.

The correction geometry to be considered is presented in figure 8. The method accounts for the range of momenta that may contribute to the signal $I$ of an ion with momentum $p$. By reducing the geometry of the TOFMS to its simplest equivalent form, we can see that it is possible for an ion with momentum $p'$ and initial angle $\gamma$ with respect to the TOFMS axis (where $p' > p$ and $\gamma > 0^\circ$) to contribute to the signal of the ion with momentum $p$. This is because the detector only resolves the component of $p$ parallel to the axis. We can calculate the maximum angle $\alpha$ at which any ion will pass through the aperture with momentum $p/\cos \alpha$, and scale $I$ at $p$ by the ratio $C$ of the area $S$ to the area of the hemisphere of radius $p/\cos \alpha$. The area $S$ is defined by the rotation of $p \tan \alpha$ over all azimuthal angles. The functional form of this correction is shown in figure 8 for the O$^{2+}$ ion, and is referred to as the ‘finite-angle correction’, as there is a finite angle that the initial momentum of an ion may make to the TOFMS axis and be detected. The correction factor reduces to $C = q \sin^2 \alpha$, where $q$ is a constant of proportionality. Also shown in figure 8 is the variation of a correction derived simply by considering the solid angle of the maximum acceptance angle for an ion with momentum $p$. This intuitive solid-angle correction is unphysical, particularly for low momentum (for the O$^{2+}$ ion, we classify low momentum when $p < 3 \times 10^4$ amu ms$^{-1}$), where the correction is independent of momentum. The finite-angle correction is the best single-step correction method possible; to improve the precision of this process, an iterative approach would be necessary.

Figure 9 shows the result of applying the correction procedure to the IMI plots from figure 7. The fully resolved distributions of the fragment ions are now observed for the first time. The most striking effect of applying the finite-angle correction is for the carbon ions. The peaks in the ion signal are now found at $p = 50, 120$ and $180 \times 10^3$ amu ms$^{-1}$ for C$^+$, C$^{2+}$ and C$^{3+}$ respectively, as opposed to at zero momentum as in figure 7. In figure 9(b), a contribution to the C$^{2+}$ ion from the overlap with the O$^{2+}$ ion has been subtracted, using the O$^{2+}$ ion signal reflected about $t(p_0)$ and scaled using the ratio of the O$^{2+}$ to O$^{2+}$ signals. As before, the carbon ions are emitted perpendicular to the laser polarization. The correction procedure is less dramatic in the case of the oxygen ions except for the low-energy O$^+$ ion.

There is some ion signal parallel to the polarization direction on the C$^+$ IMI (figure 9(a)). Although it is tempting to interpret this as the consequence of molecules being aligned perpendicular to the laser polarization, and link it with the inner ring on the O$^+$ IMI (figure 9(d)), the O$^+$ signal does not vary as a function of angle in the same way as the C$^+$ signal. As discussed earlier, the inner ring on the O$^+$ IMI plot is most likely to be due to CO$^{2+}$. The momentum of C$^+$ parallel to the polarization direction is consistent with enhanced ionization of a carbon monoxide ion CO$^+ \rightarrow O^+ + C^+$. This correlation cannot be seen on the covariance map, as it overlaps the correlations that form the (1, 1, 1) channel. To resolve this channel, we would have to calculate the triple-covariance coefficient. This could result from a sequential process beginning with the enhanced ionization of the carbon dioxide ion: CO$_2^+ \rightarrow CO^+ + O^+$. If the CO$^+$ ion remains stable, and then begins to dissociate, the first O$^+$ ion may have moved sufficiently far away that it does not play any part in the dissociation process. The dissociation
of CO$^+$ then initiates enhanced ionization CO$^+$ $\rightarrow$ C$^+$ + O$^+$, in which the C$^+$ fragment moves along the polarization direction. However, in a 55 fs laser pulse this is not possible, as the CO$^+$ and O$^+$ fragments will not have moved far enough apart to allow the C$^+$ ion to avoid interaction with the first O$^+$ ion. Alternatively, the CO$^+$ ion may originate from the CO$^+$ + O channel in a region of low intensity. In this case, the CO$^+$ ion can dissociate more rapidly, as the neutral oxygen does not strongly interact with the carbon ion. This sequential process is dominant for long-pulse experiments [4], but only a residual signal can be seen at 55 fs, and then only for the (1, 1) channel of CO. Multiple ionization during the dissociation of CO$^+$ is not possible, as it originates from a low-intensity region. Clearly, in regions of high peak intensity, CO$_2$ may be formed in an electronic level which would dissociate into CO$^+$ + O, but as the laser field rises quickly there is insufficient time for the O-CO$^+$ bond to expand before further ionization and dissociation takes place. This leads to the high-order Coulomb channels which result in three atomic ions with clearly correlated momenta.

A qualitative interpretation of the IMI plots in figure 9 can be drawn from the fact that the carbon ion distributions are not peaked at $p_0$. The molecule must have a bend-angle distribution peaked at some angle $\theta \neq 180^\circ$ at the time of the Coulomb explosion. Furthermore, the linear configuration is very unlikely, as there is little ion signal at zero momentum in the case of the three carbon ions.
Figure 9. IMI plots for the Coulomb explosion of carbon dioxide following the correction of the data. The arrow indicates the laser polarization direction. The signal at high momentum along the laser polarization in (a) and (h) is due to the overlap of adjacent ions, as in the 'ring' around the circumference of (d).
3. Monte Carlo simulation of Coulomb explosion in carbon dioxide

By employing a Monte Carlo technique to generate IMI plots from triangular distributions of bond length, bend angle and angle of alignment with the laser polarization, a comparison can be made directly with the corrected data [12]. Two independent functions represent the O–C–O bend angle (θ) and O–C bond length (r); these coordinates are illustrated in figure 10. Using values randomly derived from these functions, the positions of each ion are calculated in Cartesian space, and are allowed to explode under the Coulomb force. The result of a single simulation is a momentum vector for each of the three fragment ions O(q₁), C(q₂) and O(q₃) with charges q₁, q₂ and q₃. Rotating the three momentum vectors according to a third distribution then simulates the alignment (φ) of the molecule with respect to the laser field; this coordinate is also shown in figure 10. The r and θ distributions used in the simulation are described by three parameters: peak position, positive- and negative-going half-width-at-base (HWAB), while the φ distribution is described just by a HWAB. The r distributions determined from the present covariance experiment were used as a starting condition in the simulation process. In this work, equal bond lengths were used to simplify computation.

We were able to apply a number of initial constraints to the distributions. The φ distribution must peak at φ = 0° to constrain the oxygen ions parallel to the laser polarization. The θ distribution must peak at an angle θ ≠ 180° to reproduce the observed momenta of the carbon ions. As each simulation is equivalent to the fragmentation of one molecule, 10⁶ explosions were simulated to generate IMI plots that are directly comparable with the experiment. The main objective was to simulate all the channels observed in the present covariance mapping experiment (table 1). For completeness, the other explosion channels observed in [7,9,18] were included, which are unresolved in this work due to an overlap in the covariance islands. The distributions were varied until all of the ions from a particular channel were visually judged to be close to the experimental data. Making a visual comparison between the observed and simulated data gave a good first-order agreement. IMI plots were then generated for each ion built up from all contributing channels scaled independently. The values of these scaling parameters were found using least-squares fitting, by comparing the observed and simulated plots. Finally, the least-squares value was further improved by varying the r, θ and φ distributions and scaling values. A large number of different distributions were tested during the simulation process, to ensure that the best possible combination of distributions was found. During the simulation process, it was found that the oxygen ions were most sensitive to variation in the r and φ values, whereas the carbon ions were influenced most by variation in the peak in the θ distribution.

Figure 11 shows a graphical comparison between the experimental data and the best-fit
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This clearly shows the success of the simulation process, as the major features are well reproduced. Two simulated rings representing CO$_{2}^{+}$ and CO$_{3}^{+}$ were also included in figure 11(d) to aid visual comparison. The largest difference is in the polar width of the carbon ion signal, which is narrower in simulation. This difference could be evidence for partially sequential dissociation. An attempt was made to reproduce this by simulating non-equal bond lengths, but the results were very similar to those in figure 11. It seems that to improve the simulation process, it would be necessary to simulate the molecular dynamics before the final ionization stage is reached. These processes were not taken into account in the simulation, which starts with stationary ions.

The best-fit $r$, $\theta$, and $\phi$ distributions are presented in figures 12 and 13. Examining these results in detail, the HWAB of the $\phi$ distribution decreases from 30° for the (1, 1, 1) channel to 20° for the (3, 3, 3) channel. This agrees well with our previous work at $7 \times 10^{15}$ W cm$^{-2}$ with 60 fs laser pulses [13]. We previously attributed this narrowing to the increasing dominance of molecular reorientation. However, it now appears (as shown in section 2.3) that although laser-induced reorientation does occur for the Coulomb channels, this narrowing is due to the increasing significance of preferential ionization with channel. By comparison, Cornaggia [6] found a HWAB of 60° for the (1, 1, 1) channel, decreasing to 30° for the (2, 2, 2) channel. This difference in the width of the $\phi$ distributions may be due to the effect of laser induced reorientation. This is because the laser intensity increases from $1 \times 10^{15}$ [6] to $7 \times 10^{15}$ [13] and $3 \times 10^{16}$ W m$^{-2}$ in this work, but the effect of preferential ionization has been shown to cause widening of angular distributions with increasing laser intensity [20].

The most probable value of $r$ does not vary a great deal with channel but the distributions do narrow with increasing channel and this may have a number of physical reasons. Firstly, if we assume that enhanced ionization [1–3] is the underlying reason for the appearance of the critical distance at around double the equilibrium inter-nuclear separation, then it is possible that the ionization rate varies more rapidly for the higher charge states than for the lower charge states. Secondly, partially sequential dissociation processes can play a part in widening the bond lengths of the lowest Coulomb channels. This can be understood by assuming a simple model in which the initial dissociation of CO$_{2}^{+}$ is on a path which would lead to a molecular and atomic fragment such as CO$_{2}^{+} \rightarrow$ CO$^{+}$ + O. In a region of low intensity this may in fact be the final channel, but at a slightly higher intensity as CO$^{+}$ + O passes through $r_c$ a second ionization takes place producing CO$^{+}$ + O$. If the molecular fragment also starts to dissociate then CO$^{+}$ $\rightarrow$ O$^{+}$ + C can also pass through a second $r_c$ to give CO$^{+}$ $\rightarrow$ O$^{+}$ + C$^{+}$ and a final (1, 1, 1) channel in which one bond is longer than $r_c$. This will happen regardless of whether the second dissociation takes place before or after the first $r_c$ is reached, and the net result is a broadening of the bond lengths for the (1, 1, 1) channel. The effect becomes progressively less for increasing channels, until, for the highest channel, the second dissociation is initiated by the laser soon after the first. This leads to a more synchronized extension of the bonds: multiple ionization takes place until $r_c$ is reached where the final ionization occurs, giving a narrower observed distribution of $r_c$.

It is interesting that in this model the stability of the CO$^{+}$ ion determines whether the final dissociation channel is (1, 1) or (1, 1, 1), as the dissociation of this ion initiates enhanced ionization. This argument does not require that the two processes occur in regions of different peak intensity, merely that there is competition between the dissociation channels. Recently, Hering and Cornaggia [10] have shown, by comparing the saturation points for the oxygen ions in the (1, 1) and (1, 1, 1) channels, that these two channels originate from the same spatial region. They concluded that the (1, 1, 1) channel must result from simultaneous double ionization of CO$_{2}^{+}$. In an atomic system, the existence of doubly and triply charged ions in the same focal region would be a good indicator that the triply charged ion has resulted from
Figure 11: Comparison between the corrected experimental (EXP) and simulated (SIM) IMI plots, with the laser polarization direction indicated by the arrow.
Laser-induced Coulomb explosion in carbon dioxide

Figure 12. Bond length, $r$ ($\text{Å}$), and alignment, $\phi$ (degrees), distributions used to generate the best-fit IMI plots shown in figure 10. The variation of bond length with explosion channel is shown in the upper panel, where the peak in the distribution is shown by $r_{\text{AV}}$. The points at which these distributions fall to zero, $r_{\text{MIN}}$ and $r_{\text{MAX}}$, are also shown. Similarly, the variation in the width of the alignment distribution with channel is shown in the lower panel, where the point at which the alignment distribution falls to zero is shown by $\phi_{\text{MAX}}$. A schematic representation of the $r$ and $\phi$ distributions for the $(3, 3, 3)$ channels is included in the two small panels on the right-hand side of the figure. The $x$-axis shows the probability of a particular bond length or alignment angle, shown on the $y$-axis.

simultaneous double ionization. However, this is not the case for a triatomic molecule, in which it is the competition between partial and full dissociation, which leads to different amounts of enhanced ionization from the same focal region.

The best-fit $\theta$ distribution is shown in figure 13, where it is compared with a calculation of the ground state zero-point distribution of the neutral molecule [24], the work of Cornaggia [6] using a 150 fs laser pulse, and the result of HCl impact [18]. The ‘image’ of the molecule which results from this work is somewhat closer to the theoretical curve than in the longer pulse experiment, but for the HCl impact for which the interaction time is a few femtoseconds [18] the observed $\theta$ distribution is closer to the zero-point distribution than in this work. The present triangular distribution differs considerably from that of [6]. Physically, the probability of finding a molecule with a bend of $180^\circ$ must be zero as there is no phase space at $180^\circ$, and the fact that the bend distribution of [6] peaks at $180^\circ$ either indicates that straightening has occurred for the longer pulse, or that a deliberately simple distribution was used for ease of computation. The peak in the present distribution is $171^\circ$ compared with $174.7^\circ$ in the theoretical curve. The least-squares fitting procedure is sensitive to the peak position, to within a few degrees indicating the importance of enhancement to the bend angle and not straightening. The width of the present distribution is less than that of [6] and this is probably a more significant comparison, indicating that modifications to the molecular geometry increase
with the length of the molecule–e field interaction. This trend seems reasonable in the case of laser-induced multiple ionization and dissociation, as the probability of exciting electronic states, which change the molecular geometry, will depend on the amount of time for which the molecule is exposed to the laser pulse before Coulomb explosion occurs. This is supported by our recent results with H$_2$O [12] where, with similar techniques and pulse length, we were able to show that the molecule straightened significantly, due to single-photon bond-angle softening. This result contrasted with an earlier HCI impact experiment [25], using O$^+$ impact at 126 keV, which found that the molecule retained a significant bend similar to that predicted for the molecular ion.

4. Conclusion

A variety of experimental techniques have been used to probe the dynamics of the dissociation and subsequent Coulomb explosion of carbon dioxide on a femtosecond timescale. Firstly, covariance mapping has allowed identification of the Coulomb channels and measurement of the kinetic energy released. These results indicate that ionization takes place when the inter-nuclear bonds are around double their equilibrium ground state length. However, when a comparison is made between the present results and experiments employing a variety of pulse lengths [7,9,10], a gradual increase in KER with decreasing pulse length is evident from the increase in $k^v$. Both of these observations are consistent with the enhanced ionization. Furthermore, the results from HCI impact [18] indicate that the critical distance may be overcome with a laser pulse of a few femtoseconds duration.
Secondly, by comparing the ion signals recorded with circular and linear polarization, we have demonstrated experimentally for the first time that laser-induced molecular reorientation occurs for carbon dioxide, and that this process happens on a femtosecond timescale. The strength of the reorientation process appears to decrease with increasing Coulomb channel, indicating that the evolution of the laser-induced dipole moment depends on the stability of the molecule.

The ion-momentum imaging technique (coupled with a correction for the instrument behaviour) has proved to be a powerful tool in understanding the dissociation dynamics of CO$_2$. Firstly, we have been able to accurately determine that laser-induced reorientation only aligns the molecule to be parallel with the laser polarization direction [13]. In so doing, we have identified a residual signal from stable CO$^{2+}$, along with a signature of enhanced ionization of CO$^+$ during dissociation. Both of these result from CO$_2$ dissociating into CO$^+$ and a neutral oxygen fragment, and the stability of the nascent CO$^+$ ion governs the path into either the (1, 1) or (1, 1, 1) channels. This implies that the (1, 1, 1) channel need not be produced in simultaneous double ionization [10]. Moreover, it is worth noting that the dissociation of the CO$_2$ molecule is to be expected, as electronic levels leading to break-up will be accessed during ionization. This is a well known consequence of other ionization processes, such as electron impact [26] or synchrotron ionization [27], as well as being observed for long-pulse (tens of picoseconds) laser ionization [2]. The expansion of the inter-nuclear bonds is thus a natural mechanism in the CO$_2$ ion; hence, a search for processes that stretch the molecular bonds, such as centrifugal force due to laser-induced reorientation [10], is likely to be fruitless. The dissociation of the molecule is effectively imaged at the critical distance due to the enhanced ionization process.

Finally, the comparison of measured and simulated IMI plots has shown that carbon dioxide does alter its geometry during the reorientation–dissociation process. The zero-point bend distribution of the neutral molecule is not fully maintained throughout Coulomb explosion. It does appear, however, that the amount of the laser-induced bending, which occurs on a longer timescale [6], is less for the present 50 fs pulse. The observation of such modifications depends on a combination of the inertia of the molecule and the electric field rise time. Hence, for a laser pulse of similar rise time, it is possible to observe considerably more modification to the structure of the lighter H$_2$O molecule [17]. It is likely that modifications to molecular geometry result largely from accessing electronic levels that induce nuclear motion, as in the case of H$_2$O; however, the partially sequential nature of the dissociation process highlighted in this work, particularly for the (1, 1, 1) channel, is also a mechanism for blurring the molecular 'image' by allowing parts of the dissociating molecule to move independently of each other.

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Note added in proof. The recent results of Hishikawa et al [28], at 100 fs, show a larger degree of geometry modification than in this work, at 55 fs, but for most channels this is less than at 150 fs, confirming the trend of reduced modification with pulse length.

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Appendix 7.8

Fast-beam study of H$_2$ ions in an intense femtosecond laser field

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Abstract. A fast beam of H$_2^+$ ions, produced from a low energy ion accelerator, has been used for the first time in intense laser field experiments. The technique has enabled neutral dissociation products to be analysed and detected for the first time in such studies. Energy spectra of neutral and ionized fragments, product yields as a function of focused laser intensity and angular distributions of neutral dissociation products have been measured. Significant differences are observed between the present results and those obtained from experiments involving neutral H$_2$ molecules. These differences are indicative of the precursor H$_2$ molecule playing an important and hitherto neglected formative role in the laser-induced fragmentation processes.

1. Introduction

The continual development of high power (> 10$^{13}$ W cm$^{-2}$), short pulse (< 100 fs) lasers, coupled with advances in experimentation have opened up new areas of study in the behaviour of matter in strong fields. Over the past decade this has led to the elucidation of phenomena such as above threshold dissociation (Giusti-Suzor et al 1990), bond softening (Bucksbaum et al 1990) and bond hardening (Yao and Chu 1993, Frasinski et al 1999) in molecules, and the emission of highly energetic ions (Hutchinson 1998) and coherent x-rays (McPherson et al 1994) from rare gas clusters. Most recently the fusion of nuclei in deuterium clusters has been witnessed (Ditmire et al 1999).

The study of molecules with a limited number of degrees of freedom has been particularly fruitful, since state-of-the-art lasers deliver radiation fields comparable in strength to internuclear bonding fields. Furthermore, pulse durations of the order of tens of femtoseconds are readily generated, which are comparable to the vibrational periods ($T$) of motion, e.g. I$_2$ ($T = 155$ fs) and H$_2$ ($T = 20$ fs). This can allow both the natural rotation and vibrational motions to be frozen during the interaction of the molecule with the laser pulse. As well as the fundamental interest of intense field–molecule interactions, such studies are driven by the quest to control chemical dynamics via the variation of laser parameters such as intensity, pulse duration, phase and frequency. By far the greatest effort to date has been expended on the study of the H$_2$ molecule, this being the simplest neutral molecular system. Studies prior to 1995 have been comprehensively reviewed by Giusti-Suzor et al (1995), with more recent review papers by Codling et al (2000) and Bandrauk (2000). There have been several
Figure 1. Proton kinetic energy spectrum resulting from the fragmentation of neutral H$_2$ molecules. Peak A corresponds to the so-called bond softening peak, peak B to the so-called above threshold dissociation peak and peak C to the Coulomb explosion or dissociative ionization peak. The spectrum is typical of that observed in other such measurements (see for example Gibson et al 1997).

recent investigations of laser-produced fragmentation of the neutral H$_2$ molecule (e.g. Shao et al 1996, Thompson et al 1997, Zhu and Hill 1997, Gibson et al 1997, Walsh et al 1997 and Frasinski et al 1999) using both single colour and phase-control two colour photodissociation in which the fragmentation channels (0,1) and (1,1) were monitored. The channel notation (p,q) denotes the ionization multiplicity of the fragmenting particles.

1.1. Fragmentation of H$_2$

A measured energy spectrum of product protons resulting from the fragmentation of H$_2$ molecules by a laser pulse of wavelength 790 nm, pulse duration 65 fs and intensity $3 \times 10^{15}$ W cm$^{-2}$ is shown in figure 1. This measurement, carried out as part of the present study using the ASTRA laser at RAL (UK), utilized a gas target fed into the interaction region via a hypodermic needle in a similar way to previous studies. The spectrum shown in figure 1 is typical of previously observed H$_2$ spectra. The three observed peaks have been interpreted as being due to bond softening† (peak A), above-threshold dissociation (peak B) and Coulomb explosion (peak C). The bond softening mechanism may be understood in terms of an adiabatic avoided curve crossing between the two lowest electronic states of the H$_2^+$ molecular ion (1s $\sigma_g$ and 2p $\sigma_u$), coupled via a single photon absorption resonance, see figure 2. Ions in the vibrational level $v = 5$ of the 1s $\sigma_g$ state can escape through the gap with close to zero dissociation energy, while those in higher vibrational levels will escape with correspondingly

† Frasinski et al (1999) have recently proposed that interaction between the one photon and three photon dressed states can lead to the production of low energy protons from vibrational levels $v = 3$ and 4 via a process of bond hardening, thus providing an alternative interpretation of peak A.
Fast-beam study of H\textsubscript{2}\textsuperscript{+} ions

higher energies. A similar avoided crossing at the three photon absorption resonance (with one photon re-emitted, leading to a net two photon process) has been invoked to explain the above threshold dissociation peak, B (Zavriyev et al 1990). The position of experimental peak B has been modelled satisfactorily as resulting from excitation to the vibrational levels \( v = 1-4 \) of the H\textsubscript{2}\textsuperscript{+} ion. However, less success has been achieved in modelling the intensity and width of peak B where it is assumed that the ion is populated in a Franck-Condon distribution (Dunn 1966).

The Coulomb explosion peak, C, is believed to result from enhanced ionization, subsequent to dissociation, at some critical internuclear separation, \( R_c \), of the H\textsubscript{2}\textsuperscript{+} ion, where \( R_c > R_0 \) (the equilibrium internuclear separation of the molecular ion). The value of \( R_c \) has been predicted by the electron localization model (Seideman et al 1995i, Posthumus et al 1995), and by consideration of the charge resonance nature of the 1s \( \sigma_g \) and 2p \( \sigma_g \) H\textsubscript{2}\textsuperscript{+} states (Zuo and Bandrauk 1995). In an alternative interpretation it has been suggested that the observed kinetic energy distribution originates from ejected-electron screening of the escaping fragments, rather than due to enhanced ionization at some critical distance (Brewczyk et al 1997).

1.2. Fragmentation of H\textsubscript{2}\textsuperscript{+}

Experiments with H\textsubscript{2}\textsuperscript{+} molecular ions in intense laser fields are recognized as being particularly difficult, hence all experimental work to date has used H\textsubscript{2} as the primary target, complicating the understanding of the fragmentation dynamics of H\textsubscript{2}\textsuperscript{+}. The H\textsubscript{2}\textsuperscript{+} ions have thus been produced by laser-induced ionization via:

\[
H_2((1s \sigma_g)^2, v) + n\hbar\omega \rightarrow H_2^+(1s \sigma_g, v) + e
\] (1)
'followed' by laser interaction with the H$_2^+$, the secondary target, by the same laser pulse. The product H$_2$ ions are generally assumed to be in a Franck–Condon vibrational distribution (Gibson et al 1997). This assumes that the H$_2$ molecule remains unaffected prior to ionization in the laser field. In addition, the ejected electron is highly correlated with its parent H$_2^+$ and may influence the nascent ion before laser-produced dissociation (0, 1) and dissociative ionization (1, 1) occur.

In order to decouple these two steps, and also to shed light on the behaviour of the H$_2$ neutral in the laser field, we herein report on the first experimental study of the interaction of high intensity short pulse laser radiation with H$_2^+$ molecular ions in a fast-beam target. By using this approach the precursor H$_2$ neutral state and any electron–H$_2^+$ correlation effects associated with the primary H$_2$ ionization are avoided. Furthermore, the technique has an added advantage in that as well as detecting the product protons it also permits the detection of the product neutral H atoms. This is the first time that neutral dissociation products have been detected in the study of molecules in strong laser fields. A preliminary account of some of this work has been published previously as part of conference proceedings (Williams et al 1999, McKenna et al 1999).

2. Experimental approach

The experimental arrangement (see figure 3) will be discussed in detail in the future communication, so only a brief account will ensue. H$_2^+$ ions were formed in a plasma discharge ion source, with a 1 keV beam extracted and momentum analysed. The vibrational distribution of the ions was not measured, but running the discharge under vastly different source conditions produced no observable change in measurements. Furthermore, measurements of proton energy spectra from H$_2$ fragmentation in various gas targets have been shown to give consistent results with discharge and electron-impact type sources, where the latter is run so as to produce a classic Franck–Condon vibrational distribution (Caudano and Delfosse 1968).

At the point of interaction, the H$_2^+$ ion beam of diameter 1 mm full width at half maximum (FWHM) was intersected at 90° by a linearly polarized laser beam. The Ti:sapphire laser operated at a fundamental wavelength of 790 nm (1.6 eV), delivering pulses with an approximately Gaussian temporal profile of 65 fs FWHM at a repetition rate of 10 Hz. A lens of focal length 25 cm was used to focus the beam to a Gaussian waist of 10 μm with a maximum intensity of $5 \times 10^{15}$ W cm$^{-2}$. With the axis of polarization set mutually perpendicular to both beams, proton fragments, predominantly ejected along the polarization vector, were energy analysed by applying a variable electric field across a pair of deflection plates. The

![Figure 3](image-url)
energy-selected protons were then deflected in a 45° parallel plate analyser and detected in an off-axis channel electron multiplier. The parallel plate analyser served to separate and baffle the primary H$_2^+$ beam from the proton signal. As well as the energy analysis, a time-of-flight analysis was also incorporated into the spectrometer in order to enhance the signal to noise ratio, the noise being dominated by the interaction of the primary H$_2^+$ beam with the background gas. For each proton energy, the peak in the time-of-flight spectrum was integrated to yield a single point in the proton energy spectrum. H atom fragment yields were measured by rotating the axis of polarization of the laser through 90°, such that the polarization direction was collinear with the ion beam axis. The fast neutral products passed undeflected through the parallel plate analyser and were detected in an on-axis channel electron multiplier. In this way a complete energy spectrum for the H atoms could be deduced from a single time-of-flight spectrum.

3. Results and discussion

Measured energy spectra for both proton and H atom fragments from an H$_2^+$ molecular ion beam are shown in figure 4, with the measurements carried out at a laser pulse intensity of $3 \times 10^{15}$ W cm$^{-2}$. The intensity was calibrated by introducing Ar and Xe gas into the interaction region via a hypodermic needle, and extracting product ions into the time-of-flight spectrometer. Intensity values obtained by comparison with the threshold intensities of Augst et al (1989) agreed well with values calculated from the known laser parameters. The similarity between the normalized main peaks in the proton and neutral spectra of figure 4 is immediately
apparent. The proton peak is narrower than the neutral H peak due to a reduction in the effect of the broadening that arises from the finite velocity spread in the incident ion beam. This is the case since protons ejected perpendicular to the ion beam are analysed, whilst analysis of H atoms occurs for those ejected parallel to the incident beam. Clearly these peaks are both due to the (0, 1) dissociation channel, leading to a proton and a H atom with equal kinetic energy.

It should be noted that the proton energy calibration is due to a calculation based on the ideal action of the energy analyser, ignoring any inhomogeneity in the electric field at the edges of the deflection plates. On the other hand, the neutral H energy calibration is direct and highly accurate, relying solely on precise timing information and measurement of the distance between the point of interaction and detector. However, as can be seen in figure 4, the dissociation energy as derived from neutral and ion results are in good agreement, from which we measure a total peak dissociation energy release of 0.4 eV for the (0, 1) channel. The peak centred at ~2.0 eV in the proton spectrum, and absent in the neutral spectrum, is clearly due to Coulomb explosion, channel (1, 1), giving a total peak ionization energy release of ~4.0 eV.

In comparing figures 1 and 4, for the interaction of H\textsubscript{2} neutral molecules and H\textsuperscript{+} molecular ions respectively, with similar laser pulses, a significant difference is immediately apparent. The two proton peaks A (one photon) and B (two photon) centred close to 0 eV and at 0.5 eV respectively for H\textsubscript{2} (figure 1) have been replaced by a single dissociation peak centred at 0.2 eV for H\textsuperscript{+} (figure 4). Although this peak is quite broad in energy, the position of the peak suggests that the one photon process is dominant in the present measurements, with the possibility of some contribution from the two photon process. This is the exact reverse of the observation in neutral H\textsubscript{2} targets at similar intensities. It is also worth noting that the neutral spectrum in figure 4 provides the first opportunity to observe a three photon peak, predicted to occur at a fragment energy of 1.3 eV. This is due to the absorption of three photons, but avoiding the re-emission of one photon as happens in peak B. In high pulse intensity experiments such a peak would always be hidden below the Coulomb explosion peak in a proton spectrum, but if present would be evident in a neutral spectrum. In the present study there does appear to be a distinct shoulder on the high energy tail of the (0, 1) H atom spectrum which could be indicative of a three photon process.

To further investigate the question of multiphoton processes the product yield as a function of laser pulse intensity was studied. In figure 5, currently measured fragment yields for protons and H atoms resulting from the dissociation of H\textsuperscript{+}, and protons resulting from the ionization of H\textsubscript{2} are shown. Again, measurements of both dissociation products are in good agreement, with the dissociation channel (0, 1) unsaturated even at the highest intensity. The (0, 1) and (1, 1) channels have also been studied by Gibson et al (1997) with both channels displaying an intensity dependence of slope $n = 3$, indicative of initial three photon absorption. However in the present work we observe for the (0, 1) channel a slope close to unity, confirming the dominance of a one photon process. It is thus quite clear that any contribution from three photon absorption (leading to either a two or three net photon process) to the (0, 1) peak in figure 4 is very small. It must be emphasized that while previous work at low intensities has shown a domination of a one photon process (Zavriyev et al 1990), this has never previously been seen at higher intensities in association with Coulomb explosion. In addition, in the current work the (1, 1) channel also displays the same $n = 1$ dependence. The fact that in both the present work and in that of Gibson et al (1997) the ionization channel follows the same photon absorption dependence as the dissociation channel, provides confirmation that the Coulomb explosion reaction does follow initial dissociation.

The absence of a strong signal from a three photon absorption process in both the energy spectra and the intensity dependence of fragmentation channels of the H\textsuperscript{+} ion indicates that the observed three photon spectra from H\textsubscript{2} are strongly correlated with processes in the neutral
molecule. Such precursor processes in the neutral $H_2$ molecule could be due to the 'first ionized' electron wavepacket, produced in the leading edge of the pulse but trapped in the oscillating laser field repeatedly returning close to the ionic core over a number of optical cycles. This phenomenon has been shown to account for such diverse processes as high harmonic generation (Corkum 1993), dissociative recombination (Talebpour et al 1996) and non-sequential ionization (Corkum 1993, Becker and Faisal 1999). In addition, bond softening may be occurring in the $H_2$ neutral molecule itself, increasing the internuclear separation prior to ionization, resulting in the $H_2^+$ ion being formed predominantly in vibrational states $v < 5$ due to the modified Franck–Condon overlap. Hence for 790 nm laser pulses, dissociation of the $H_2$ ion via bond softening could not energetically proceed through one photon absorption, and would thus be dominated by a three photon process. Bond softening of the precursor neutral is implicit in the argument of Frasinski et al (1999), supporting their assertion of formation of $H_2^+$ ions in a limited number of vibrational levels ($v = 3, 4$) leading to bond hardening.

In the present study the population of the vibrational levels in the $H_2^+$ 1s $\sigma_g$ state, resulting from production in a discharge type ion source, is believed to be close to the classical Franck–Condon distribution. However, even though levels $v < 5$ are thus expected to be heavily populated, there is no indication of significant dissociation occurring from these levels. Hence it would appear that the probability of three photon absorption is much less than for one photon absorption, even at pulse intensities where Coulomb explosion occurs. This again implies that those levels $v < 5$ are preferentially populated in experiments starting from the neutral molecule in order to reverse this propensity. In the inset of figure 4 we have plotted the (0, 1) dissociation peaks on an expanded energy scale, and fitted a Franck–Condon vibrational distribution for the one photon process, arbitrarily normalizing to the experimental data at $v = 9$. It is apparent that the higher vibrational levels are present in the primary beam, and perhaps not surprisingly appear to fully dissociate. The degree of dissociation falls away for vibrational levels $v < 8$. 

Figure 5. Fragment yield as a function of laser intensity. □, $H$ yield from the dissociation channel (0, 1); ▲, $H^+$ yield from the dissociation channel (0, 1); ●, $H^+$ yield from the dissociative ionization channel (1, 1).
In addition, by rotating the laser polarization from 0°, where the polarization axis is parallel to the incident ion beam, through 360° in steps of 4°, we have measured the intensity of product H atoms as a function of angle, θ, with respect to the direction of polarization (see figure 6). This indicates a cos²θ distribution, in marked contrast to the cos⁶θ distribution (n = 7) observed for experiments with a primary H₂ neutral molecule (Thompson et al 1997). The higher the value of n the greater the degree of alignment of the molecular axis with respect to the laser polarization direction, and it has been shown to correspond to a reorientation of the molecular axis in the intense field. In the present case the value of n = 2 suggests that no reorientation of the H₂ molecular ion occurs in the dissociation process, the cos²θ distribution merely mirroring the fall in |E|² (where E is the laser electric field vector) in the direction of the detector. It is likely that the H₂ ions in the present study dissociate at an early stage on the rising edge of the laser pulse through the one photon process, allowing insufficient time for reorientation with the E vector to take place. In experiments using H₂ as the primary species, the molecular ion dissociates predominantly via a three photon absorption process at these high laser intensities. It would thus appear that the neutral molecule itself aligns in the laser field prior to or during the initial ionization. This results in an oriented H₂⁺ ion which is able to absorb three photons with high efficiency due to the alignment of the dipole moment with the field. The lack of alignment in the present study could explain the apparently low yield of...
dissociation products arising from initial three photon absorption. There is thus compelling evidence that alignment is present in the neutral molecule, consistent with an emerging picture of the laser-induced dynamics of neutral molecular species playing a significant role in the subsequent ion dynamics (Larsen et al. 1999, Bryan et al. 2000). It is again indicative of the active role played by the neutral precursor in the laser field.

Finally, the Coulomb explosion energy spectrum of figure 4 has been transformed to display the ionization rate of the (1,1) channel as a function of internuclear separation $R$. Figure 7 shows that the rate is in reasonable agreement with the theoretical prediction of Zuo and Bandrauk (1995), and with a previous experiment in neutral H$_2$ (Gibson et al. 1997) where meticulous care was taken to operate below the saturation intensity for the ionization of H$_2$ and H$_2^*$. The ionization is shown to occur predominantly around a critical distance of $\sim 7$ au in good accord with the theoretical predictions (Seideman et al. 1995, Posthumus et al. 1995, Zuo and Bandrauk 1995). There is no evidence to support a second critical distance at 10 au as postulated by Zuo and Bandrauk (1995), although the statistical uncertainty in the experimental data at this point is such that further confirmation is desirable.

4. Conclusion

In conclusion, we present the first experimental results for the dissociation and ionization of a beam of H$_2^*$ molecular ions in an intense laser field. We also present the first energy spectra of neutral dissociation products in such strong field studies. Significant differences with proton energy spectra obtained from neutral H$_2$ molecules under similar laser conditions suggest that the neutral parent plays an important precursor role in the laser-induced fragmentation dynamics of H$_2$. We postulate that this effect may be due to electron correlation and/or bond softening of the primary neutral molecule, and strongly encourage theorists to explore the possibilities. Furthermore we present evidence that the H$_2^*$ molecular ion does not undergo
reorientation prior to one photon dissociation, and suggest this is indicative that in previous studies reorientation of the neutral H₂ molecule was significant.

Much of the understanding of fragmentation processes in intense laser fields has been due to the interpretation of new experimental measurements rather than a priori predictions. Experimental advances, such as the use of ion beams and detection of neutral products, will further challenge the theoretical unfolding of the dissociation dynamics of both ionic and neutral species. It is thus anticipated that the use of ion beams will play a major role in the continued elucidation of this new and complex area of physics.

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Appendix 7.9

A Detailed Study of Multiply Charged Ion Production Within a High Intensity Laser Focus


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Abstract

We have observed the variation in ion signal as a function of intensity within a focused laser spot. Using an aperture detector, the ion signals from narrow bands of the laser focus have been observed. By moving the laser focus along the direction of propagation, regions of different intensities are exposed to the detector. This has allowed detailed measurements to be made of ion signals as a function of laser intensity.

1. Introduction

In the interaction of a focused laser beam of wavelength $\lambda$ with a gas target, the atoms and molecules are exposed to a range of intensities which can vary by several orders of magnitude. The observed ion signal of any particular species, is only an average over a range of intensities when the full focused spot is exposed to the detector. Using a soft focus lens i.e. large $f$-number, a relatively large focus of several mm in the $z$ direction can be produced. This allows spatial resolution of the intensity distribution by scanning a slit of width $\Delta z$ (0.5 mm) along the $z$-direction, this is illustrated in Fig. 1.

2. Laser beam characteristics

The focused laser beam intensity $I_{0}(r,z)$ is Gaussian in $r$ ($r \perp$ laser beam direction) and Lorentzian along $z$ (the laser beam direction) [1] and is given by

$$I_{0}(r,z) = \left[ \frac{I_{0}}{1 + \left( \frac{z}{z_{0}} \right)^{2}} \right] \exp \left[ -\frac{2r^{2}}{\omega_{0}^{2} \left[ 1 + \left( \frac{z}{z_{0}} \right)^{2} \right]} \right] \quad (1)$$

where $z_{0} = n_{0}o_{0}/\lambda$ is the Rayleigh range, $\omega_{0} = 2k\lambda/D$ ($D$ beam diameter before the lens) is the minimum waist radius at $1/e^2$ and $I_{0}$ is the maximum intensity. Rewriting the above equation and plotting $r$ vs $z$ for a given $I_{0}(r,z) < I_{0}$ generates 'peanut' shape contours bounded by the saturation intensity for the production of that particular ion species i.e. $A^{+}$, $A^{2+}$, $A^{3+}$ etc.

$$r = \left[ -\omega_{0} \left[ 1 + \left( \frac{z}{z_{0}} \right)^{2} \right] \ln \left[ \frac{I_{0} \left( 1 + \left( \frac{z}{z_{0}} \right)^{2} \right)^{2}}{I_{0}} \right] \right]^{1/2} \quad (2)$$

The volume that generates a given ion is that volume bounded by the saturation intensity of that ion minus the volume bounded by the saturation intensity of the next higher charge state. The computed volumes for $\text{Xe}^{+}$ to $\text{Xe}^{9+}$ are given in Fig. 2 both as a function of $z$ and $I_{0}(r,z)$.

Intensity selective scanning (ISS) using a sub-millimeter slit of width $\Delta z$ reduces the whole exposed volume to a volume slice of thickness $\Delta z$ [1,2]

$$V_{3D} = \frac{n}{2} \Delta z \Delta r \Delta z_{0} \left[ 1 + \left( \frac{z}{z_{0}} \right)^{2} \right] \ln \left[ \frac{I_{0}}{I_{0} \left( 1 + \left( \frac{z}{z_{0}} \right)^{2} \right)^{2}} \right] \quad (3)$$

3. Experimental setup

A schematic of the apparatus is shown in Fig. 3. The laser pulse (Ti:S, $\tau \approx 70$ fs, $\lambda = 800$ nm and 10 Hz) has a pulse energy of 5 mJ. Throughout the experiment, the pulse time and frequency profile was monitored using a FROG (frequency resolved optical gating) system. The laser beam was focused with a 25 cm focal length lens mounted on a computer controlled translation stage outside the experimental chamber; the focus of the laser beam is moved in 0.1 mm steps with respect to the aperture (0.5 mm). Xenon gas is introduced into the vacuum chamber, rising the press-
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Hypodermic Beam waist

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Fig. 2. Xenon ions computed volumes at $I_0 = 2 \times 10^9 \text{ W/cm}^2$ and the appearance intensity from Auget et al. [3]. Dashed curves are the full volumes bounded by each ion appearance intensity while marked solid curves are the volume slices that generate each of the ions: (a) as a function of $z$ and (b) $z$ converted to local on axis peak intensity.

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Fig. 3. Schematic diagram of the apparatus used in the ISS experiment. Xenon gas is introduced out of the page from a 0.5 mm hypodermic needle. The lens is moved with respect to the pinhole to scan the ion signal volumes. Xenon ions are extracted through the aperture by the E-field (1100 V/m) between the two plates into a time-of-flight (ToF) mass spectrometer. The ions are detected by channeltron at 26 cm from the interaction region and the signal from the ToF was fed directly into a Tektronix TDS 744A digital oscilloscope interfaced to a PC. The ToF spectrum at each translation step was averaged over 100 laser shots. A typical z-scan matrix of Xe ions is given in Fig. 4.

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Fig. 4. A typical z-scan matrix of Xe ions shows a fuller and detailed picture of the variation of Xe ions within the focused spot.

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Fig. 5. The integrated signal along the ToF axis for each type of Xe ion. The solid curves are the computed volumes where $P_{II} = 1$, diffraction limit $\delta = 1.5$ and core intensity $I_0 = 9 \times 10^9 \text{ W/cm}^2$ calculated with 85% transmission through optics.

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4. Discussion

Previous work on ISS [2] indicated a spatial dependence in ion production, however the matrix presentation yields a more complete picture of the intensity distribution within the focused volume. In order to make direct comparison of measured volumes to the computed volumes, each of the species of Xe ions have been integrated along the ToF axis. This is shown in Fig. 5 as a function of lens position along with the corresponding calculated volumes.

Only where the probability of ionization is saturated ($P_{II} = 1$) is the signal proportional to volume and the cal-
calculated volumes are representative of the observed ion signal volumes. If $I < I_{\text{sat}}$ then $P(I) < 1$. The computed curves in Fig. 5 depend not only on the values of $I_{\text{sat}}$ but also on the diffraction limit, $\delta$, of the optics employed. Ideally $\delta = 1$ but when $\delta > 1$ the effective value of $I_{\text{sat}}$ is reduced and the $I_{0,0}$ variation will change. In order to achieve the fit in Fig. 5 the values of $I_{\text{sat}}$ and $\delta$ were varied. The best fit was obtained with $\delta = 1.5$ and $I_{\text{sat}} = 2.5 \times 10^{14}$ W/cm$^2$ for Xe$^+$. Beyond the limit of the calculated volumes (e.g. $z > 5$ mm for Xe$^+$) ions show a threshold process [3] before matching to the computed curves. This slow rise in ion signal can be attributed to field ionization in volumes in the tunneling regime [3–5] ($P(I) < 1$). From Fig. 5 the $I_{\text{sat}}$ values for Xe$^+$ occur at $z = 5.2$, $3.1$, $2.0$, $1.3$ mm respectively which yield field intensities of $2.5$, $6.5$, $15$, $30$ ($\times 10^{14}$ W/cm$^2$) using

$$I_{0,0} = \frac{I_0}{1 + \left(\frac{z}{\lambda_f}\right)^2} \quad (4)$$

($I_0 = 9.1 \times 10^{15}$ W/cm$^2$). These values are higher than those quoted by Augst et al. [3] who used 1 ps pulses but are in line with the work of Christov et al. [6] who demonstrated that for short pulses the ionization saturates at higher intensities than for longer pulses. This arises due to the phase lag of the atomic dipole with the electric field.

5. Conclusion
Using ISS method, the spatial distribution of the various atomic ions within the focused laser beam yields not only the functional dependence of a signal with intensity $I$ but also the onset of saturation for each ion species and the value $\delta$ of the effective diffraction limit. This powerful technique can now be extended to the study of molecules and molecular ions in which intensity dependent ionization and dissociative ionization processes can be resolved [7,8].

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