Short Pulse, High Intensity Laser Interactions with Molecules

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Abstract

Direct measurements of the angular distributions of CO$_2$ fragment ions produced in interactions with 750 nm laser pulses of 60 fs duration are presented. These distributions dramatically show the bent nature of the initially linear dissociating molecule and allow observation of the alignment of the different dissociation channels.

The first measurements of 750 nm laser pulses of 60 fs with vibrationally excited CO$_2$ are presented. In comparison with ground state CO$_2$ enhanced kinetic energies of the carbon fragment ions, particularly C*, have been observed. These observations are consistent with unusually large bends in the molecule induced by the laser field. Perpendicular alignment of the molecule with the laser field is also implied. A comparison of the results of dissociative ionisation of CO$_2$ by 750 nm laser pulses of 60 fs duration and by 532 nm laser pulses of 35 ps duration is made.

Presented for the first time are the results of intense laser field dissociation of nitrous oxide using laser pulses of 35 ps duration and these results are compared to the dissociative ionisation using 750 nm laser pulses of 60 fs duration. Original results of MEDI of sulphur hexafluoride using 60 fs laser pulses at 750 nm are presented. The fragmentation pattern of SF$_6$ displays features similar to those found in experiments with diatomic and triatomic molecules, with a tendency towards symmetric dissociative channels and producing fragment energies which for all channels are consistent with a Coulomb explosion at a single, critical, internuclear separation.
To my Grandad,
whom I wish could have seen the completion of this work.
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Chapter 1: Introduction

1.0 Introduction

The study of intense laser field physics is a well established but fast moving and expanding field. The advent of tabletop lasers producing short pulses which can then be spatially focused to dimensions of \( \mu \text{m}^2 \) has resulted in the production of laser intensities of up to \( 10^{17} \text{ W/cm}^2 \). However, even a focused intensity of \( 10^{14} \text{ W/cm}^2 \) is considered to be super-intense.

To elaborate on the dramatic effect of these laser electric fields on atoms a comparison of the atomic field binding the electron to the proton in hydrogen atom (51.4 V/Å) and the electric field produced by the focused laser intensity \( 10^{16} \text{ W/cm}^2 \) (8.68 V/Å) show that they are comparable in magnitude. The electric field magnitude is comparable with the atomic field and can no longer be treated as merely a perturbation. Intense laser field interactions with atoms and molecules can be thought of in two ways; either as a multiphoton process or as a field ionization process. Traditionally, the Keldysh parameter, \( \gamma \) (Keldysh, 1965) is used to distinguish between the two regimes.

\[
\gamma = \left( \frac{\omega (2mE_i)^{1/2}}{eF} \right)
\]

Equation 1.1
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where $\omega$ is the optical frequency of the bound electron ($s^{-1}$), $E_1$ is the zero field ionization potential of the bound electron (J), $F$ is the peak electric field (V/m) and $e$ and $m$ are the charge (C) and mass (kg) of the electron, respectively.

The Keldysh parameter, $\gamma$, defined in Equation 1.1, is the probability of an electron escaping the potential well that is binding it to the nucleus. The potential well is a superposition of the atomic potential and the oscillating laser electric field potential. Keldysh, 1965, found that if the tunneling frequency is much less than the angular frequency of the oscillating electric field ($\gamma<<1$) then the ionization process can be envisaged as tunneling due to field ionization; however, if the opposite is the case ($\gamma>>1$) then the ionization is modeled better as a multiphoton process. More recently the boundary of the multiphoton regime has been closely examined (Ilkov et al., 1992) and the multiphoton regime found to be appropriate for $\gamma>0.5$.

**Figure 1.1:** Schematic representation of a four-photon non-resonant multiphoton ionization of an atom, where $E_i$ is the photon energy and $E_1$ is the energy required to ionize the atom.

Multiphoton ionization is the process whereby an atom with an ionization energy $E_1$, is ionized by photons with an energy $E_i$, where $E_i << E_1$, as shown in Figure 1.1. The atom, therefore, has to absorb several photons from the laser radiation in order to be ionized. This can only be achieved if the photon flux is strong enough, as in the use of high intensity pulsed lasers, such that a second photon arrives at the first photon position before the end of the lifetime, $\Delta t$, of the virtually induced state, defined by $\hbar/\Delta E$. Non-resonant multiphoton ionization rates can be predicted by Equation 1.2 (Gontier and Trahin, 1984).

$$P = \sigma N F^N$$  

Equation 1.2
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where $P$ is the $n$-photon ionization rate (s$^{-1}$), $\sigma_n$ is the generalized multiphoton cross section (cm$^{-2}$ s$^{-1}$), $I$ is the peak laser intensity (photons cm$^{-2}$ s$^{-1}$) and $n$ the number of photons absorbed.

Generally at higher intensities and/or longer wavelengths (where $\gamma << 1$) there are substantial difficulties in applying conventional multiphoton theory. Multiphoton theory assumes the laser electric field to be a perturbation. For $\gamma << 1$ this can no longer be considered to be the case. The higher order terms of the perturbation series are no longer negligible and the entire theoretical multiphoton procedure breaks down. Tunneling then becomes the dominant mechanism producing ionization of the atom. The electric field produced by the focused laser light perturbs the Coulomb potential resulting in a lowered potential barrier, as shown in Figure 1.2a. The electric field oscillation time is longer than the time taken for the electron to tunnel out of the potential well. The perturbation of the field, and thus, the reduction of the barrier, is dependent on the laser intensity and the tunneling time is dependent on the height of the barrier.

![Figure 1.2: The perturbation of the xenon atomic potential well by the intense laser electric field (the sloped linear lines) such that a) the 5p$^5$ electron remains bound and b) at a higher laser intensity it can escape classically over the barrier.](image)

Experiments began, quite naturally, by investigating the effect of exposing an atom to the intense electric field. Within the multiphoton regime perturbation theory was successful in predicting appearance intensities of ions in the field. Problems arose for physicists when performing experiments in the tunneling regime. Initially, the tunneling regime was only accessible by altering the wavelength of the laser light (Chin et al., 1988). However, later, as laser technology improved higher focused...
laser intensities were achieved pushing shorter wavelengths into the tunneling regime (Codling et al, 1987). There was also some difficulty in understanding ionization in the 'intermediate regime' where $\gamma=1$. Within this region ionization did not appear to be dominated purely by either tunneling or the multiphoton mechanism.

1.1 A Sequential Versus a Collective (Rapid Vertical) Ionization Mechanism

Intense laser field ionization produces ions in a range of charge states. What is unusual compared to electron impact ionization or synchrotron radiation ionization is that the charge states produced are so high. L'Huillier et al, 1983a and 1983b, measured the ionization rates of xenon and appearance intensities of the ions in order to investigate the mechanisms of ionization. Two possible theories were put forward to describe how ionization occurred. Firstly, that the ionization mechanism could be collective, or instantaneous, for example, $\text{Xe} \rightarrow \text{Xe}^{8+}$, with both electrons removed simultaneously from the atom, or secondly that the final ionization state was the result of a sequential, or stepwise, process where $\text{Xe} \rightarrow \text{Xe}^+$ was followed by $\text{Xe}^+ \rightarrow \text{Xe}^{8+}$ such that the ionization occurred in two stages. The experiment lead them to the conclusion that at high intensities for 532 nm and 1064 nm wavelength light the ionization mechanism was sequential, but that for low intensity light the ionization was collective. However, Boyer et al, 1984, using 193 nm light with a peak intensity of $10^{15}$ W/cm$^2$ on Ar and Kr and Luk et al, 1985, also using 193 nm light but with a peak intensity of $10^{17}$ W/cm$^2$ on He, Ne, Ar, Kr, I, Xe, Eu, Yb, Hg and U, both found no evidence of stepwise ionization and concluded that the ionization mechanism was a collective process. It was pointed out by Lambropoulos, 1985, that the laser intensity in a real situation is not a delta function but increases during the pulse. Thus, sequential ionization, with a rising laser intensity, was the only realistic explanation. Codling et al, 1987, in an effort to settle the question realized that sequential ionization could be proved or disproved by dissociatively ionizing a molecule, specifically hydrogen iodide which is isoelectronic with xenon. If collective ionization occurred at the equilibrium internuclear separation then the kinetic energy of the fragments would be large when calculated using Coulomb repulsion. In fact Codling et al, 1987, detected ionic fragments with energies lower than expected implying that Coulomb explosion occurred at larger
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internuclear separations than the equilibrium separation. This was interpreted as the result of a slow stepwise process.

The field ionization Coulomb explosion model (Codling et al, 1987) is a classical model for predicting appearance intensities of ions. The assumption is that tunneling through the potential barrier is a minor process and that most of the ionization is caused by the escape of the electron over the potential barrier. The outermost electron is positioned in the Coulomb well of the singly charged point-like core of the atom at the energy level corresponding to the ionization potential. When an electric field is applied to the atom the potential well is distorted, creating a finite width potential barrier, as shown in Figure 1.2a. In this purely classical model the barrier reduces with increasing laser intensity until finally the electron can escape over the top of the barrier resulting in ionization, as shown in Figure 1.2b. Later this model was further developed (Codling et al, 1989) to take into account the fact that the electrons can also tunnel through the barrier and, thus, it developed into a quasi-classical model. The field ionization model can be applied equally well to diatomic molecules as to atoms.

The direction of the applied laser electric field rapidly reverses direction within half the period governed by the wavelength of the laser light. For example, a laser of 750 nm reverses electric field direction every 1.25 fs and a laser of 532 nm every 0.89 fs. The field ionization Coulomb explosion model proposes that at the beginning of the ionization process the outermost electron in the diatomic molecule can move from ion to ion, but that as the ions move further apart the inner potential barrier hinders the charge transfer and the electrons become localized within one well. A new mechanism was suggested in which an electron trapped in the potential well, shown on the left of the Figure 1.3, could be ionized over the inner barrier into the continuum.
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**Figure 1.3:** Field ionization of a diatomic molecule when the laser polarization is parallel with the molecular axis. The ionization potential of the localized electron has been Stark shifted by the laser field such that it can escape from the potential well on the left-hand side of the figure into the continuum.

Frasinski et al, 1989a, explained how, using the potential energy curves shown in Figure 1.4, ionization of the nitrogen molecule could be occurring as a process of instantaneous excitation followed by dissociation to a particular internuclear distance followed by further ionizations and subsequent dissociations until the molecule was completely dissociated. The field ionization Coulomb explosion model had led the Reading group to the conclusion that sequential ionization was the most reasonable explanation of ionization in intense laser electric fields.

**Figure 1.4:** Potential energy diagram of N₂ showing the path of sequential ionization and dissociation (Frasinski et al, 1989a).

However, these experiments (Codling et al, 1987 and Frasinski et al, 1987) and the field ionization Coulomb explosion model did not settle the question of collective versus sequential ionization. Results from experiments performed by other groups
seemed to find that both collective and sequential ionization occurred under various circumstances. An experiment on the nitrogen molecule (Boyer et al., 1989) indicated that vertical transitions to higher charge states of the molecule from the equilibrium distance were occurring for intensities of $10^{16}$ W/cm² and 248 nm wavelength laser light. Frasinski et al., 1989, reanalyzed the data of Boyer et al., 1983, and showed how the results could be reinterpreted as sequential ionization. Cornaggia et al., 1990, studying N₂ using two different wavelengths, 305 and 610 nm, found that the kinetic energy of the fragment ions showed a vertical collective ionization transition from the equilibrium internuclear separation of the transient molecular ion for the former wavelength and sequential ionization mechanism at increasing internuclear distances for the latter wavelength. Normand et al., 1991, found that stepwise ionization occurred for dissociative ionization of oxygen using 600 nm laser light, but also that the ionization was collective using laser light of 248 and 305 nm, which compared well with the data from Cornaggia et al., 1990, on N₂. Commenting on Cornaggia et al., 1990, Normand explained the two mechanisms for different wavelengths by suggesting that initially the parent ion is excited to the N₂⁺ state. For the 305 nm experiment the lifetime of this state is long compared to the risetime of the pulse and therefore, the only route for ionization is a rapid vertical (collective) ionization. However, for the 610 nm light the lifetime of the transient parent ion state is short compared to the risetime of the pulse allowing sequential ionization to proceed. Normand et al., 1992a, investigating carbon monoxide found that using 2 ps 610 nm laser light and 1.4 ps 305 nm laser light the ionization was sequential. However, they noted that the kinetic energy peaks were very sharp and therefore suggested that the dissociation of the molecule between ionization steps could not take place via Coulomb dissociation curves, since broad energy distributions would be expected. They suggested that the dissociation proceeded via laser field modified resonance states.

Frasinski et al., 1991, so far an advocate of stepwise ionization, questioned this when they used a 3D covariance map to look at the fragmentation pattern of N₂O using 600 nm wavelength laser light. They suggested that six electrons were promoted to super-excited states and were stabilized by a combination of the oscillating field and the three potential wells. After stabilization was lost they postulated that the electrons were simultaneously ejected from the molecule. There was an important problem with the sequential ionization idea. It had been assumed that the particular internuclear separation for each stage of ionization was...
determined by the intensity level, and therefore a dependence of kinetic energies of the fragment ions on the risetime of the laser pulse was expected. However, experiments (Cornaggia et al., 1991, Normand et al., 1992 and 1993, Strankiewicz et al., 1993, Codling and Frasinski, 1994 and Schmidt et al., 1994) seemed to indicate that the kinetic energies were independent of the risetime of the laser pulse. This interesting development is discussed in Section 1.3.

1.2 Symmetric Versus Asymmetric Fragmentation

Two possible outcomes were initially entertained during investigations of how diatomic molecular charges are distributed over the fragment ions. Firstly, that both fragment ions have the same charge (or differ by one charge unit, in the case of an oddly charged transient ion) which is referred to as symmetric fragmentation. Secondly, that the charge states of the ions differ by \( \geq 2 \), which is referred to as asymmetric fragmentation.

The first molecule studied for the purpose of investigating the way in which molecules fragment in the intense laser field was nitrogen (Boyer et al., 1989) using 248 nm light of peak laser intensity \( 10^{16} \text{ W/cm}^2 \). They found that asymmetric channels appeared to be dominant. Analysis of their one dimensional time of flight (1D-TOF) spectra led them to conclude that they had detected (1,1), (0,2), (1,2) and (1,3) channels but not the (2,2) channel, where \( N^q+\text{N}^p \) is denoted by \( (q, p) \). They proposed that charge asymmetric fragmentation was a natural consequence of the large induced dipole moment arising from the collective motion of the electrons along the laser electric field and that this displacement of charge leads automatically to a corresponding charge asymmetry in the dissociating products. However, Frasinski et al., 1989, also investigating the nitrogen molecule but using a 600 nm wavelength, 0.6 ps pulse duration and a peak laser intensity of \( 3 \times 10^{15} \text{ W/cm}^2 \) found that symmetric fragmentation channels dominated the spectrum. Using covariance mapping they determined that the main channels were (1,1), (1,2), (2,2) and (3,3). The technique allowed the fragmentation channels and also the strength of the channels to be determined thereby eliminating some of the ambiguity of the 1D-TOF analysis. Covariance mapping also allowed the determination of the total kinetic energy release for a fragmentation channel. Normand et al., 1991, found that for wavelengths of 305 nm and 610 nm the charge
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fragmentation patterns for CO, N₂ and O₂ were asymmetric for the former wavelength and symmetric for the latter wavelength. However, when the Reading group took their covariance mapping equipment to Saclay and performed the same experiment (Codling et al, 1991) on the French equipment they found that in all cases the fragmentation pattern was symmetric.

Figure 1.5: Thomas-Fermi-Dirac model of field ionization where all three graphs are for the same laser intensity but with increasing internuclear separation of (a) 1.6 Å, (b) 2.3 Å (dissociation point) and (c) 3.0 Å (Brewczyk et al, 1991)

Brewczyk et al, 1991, presented the Thomas-Fermi-Dirac (TDF) model which was used to calculate charge states us the Fermi gas distributions. It treated the electrons as a continuous cloud distribution whose total charge need not be a multiple of the elementary charge. The external field perturbs the electron potentials and the electronic charge cloud spills over the potential barrier and the molecule becomes ionized, as shown in Figure 1.5. Branching ratios for N₂ were plotted and the theory predicted that symmetric fragmentation channels should dominate the spectrum.

Strickland et al, 1992, disagreed with the Reading group's position on symmetric charge fragmentation channels and suggested an explanation as to why they appeared to detect only symmetric fragmentation channels. Strickland et al, 1992, pointed out that using the covariance mapping technique nascent ions, produced at the beginning of the laser pulse, cannot be distinguished from ions produced much later in the pulse as secondary products from ions or atoms which have separated from the other constituents of the molecule during a primary dissociative ionization process. These ions produced later in the pulse are known as post-dissociative ionization (PDI) products. It was suggested that asymmetric fragmentation is the norm for ions produced in the initial interaction and but that at a later stage in the laser pulse the ions are further ionized so that the complete process produces products which can be erroneously interpreted as a single interaction producing a
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symmetric fragmentation pattern. To investigate this theory Strickland et al, 1992, used molecular iodine as a target gas which has a long ground state vibrational period (155 fs) in comparison to the short laser pulse (30 fs). Thus the molecule was effectively vibrationally frozen and inertially confined for the entire duration of the pulse, eliminating the possibility of PDI. As predicted, the group detected both symmetric and asymmetric fragmentation patterns.

Stankiewicz et al, 1993, reanalyzed the data from Comaggia et al, 1990 and 1992 and Lavancier et al, 1991, and was able to re-interpret the data in terms of asymmetric primary processes masked by PDI. The authors proposed that all of the data, interpreted as symmetric fragmentation channels, were actually predominantly asymmetric after the initial dissociative ionization process. However, Hatherly et al, 1994, asked that if asymmetric fragmentation was such a dominant process why was not even a trace of asymmetric fragmentation channels found using covariance mapping.

It became obvious that in order to determine the initial processes PDI had to be distinguished from them. Schmidt et al, 1994, investigated the dissociative ionization of \( \text{Cl}_2 \) for two different pulse lengths 2 ps (610 nm) and 130 fs (395, 610 and 790 nm) and found no evidence of PDI. They determined the various channels produced and the kinetic energy releases of these channels by analyzing 1D-TOF spectra. The channel energies were compared to each other to see if any were of the same magnitude as those found for lower ionization channels in order to try and deduce if PDI processes were occurring. PDI creates no further kinetic energy for the ion since it involves only removal of the electron in the flat part of the Coulomb curve. Thus, channel (2,1) could have the same energy as a channel (2,2) involving PDI of one of the ions. Schmidt et al, 1994, concluded that since they had found no evidence of PDI the observed charge symmetric channels were not due to an experimental artifact arising from PDI.

1.3 Dependence of the Channel Kinetic Energy Release on Laser Pulse Intensity and Risetime
Chapter 1

The field ionization Coulomb explosion model (Codling et al., 1987) predicts that the kinetic energies of the dissociating ionic fragments should depend on the risetime of the pulse. The scenario of dissociative ionization begins with a molecule ionizing and expanding. During the expansion the laser intensity increases with the risetime of the pulse until the intensity is high enough to cause another ionization. This process of ionization followed by expansion continues until the intensity no longer increases or until the molecule has completely dissociated. It follows that the steeper the risetime of the pulse the less the molecule will have been able to dissociate before the laser intensity is high enough to cause a further ionization. Thus, the model predicts that the kinetic energies of the resulting highly charged fragment ions are greater for a steeper laser pulse risetime.

Table 1.1: Comparison of the kinetic energy releases of fragment ions released in the dissociative ionization of the nitrogen molecule from Lavancier et al., 1991 (Ref 1), Codling et al., 1990 (Ref 2) and Cornaggia et al., 1991 (Ref 3).

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<td>2 ps pulse duration (Ref 1)</td>
<td>600 fs pulse duration (Ref 2)</td>
</tr>
<tr>
<td>N⁺</td>
<td>3.5</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>5.8</td>
<td>6.5</td>
</tr>
<tr>
<td>N₂⁺</td>
<td>6.2</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>N₃⁺</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>15</td>
</tr>
</tbody>
</table>

Cornaggia et al., 1991, compared their results to those of Lavancier et al. 1991, and Codling et al., 1990, and found that the kinetic energy releases for the dissociative ionization of N₂ did not appear to depend on the risetime of the pulse, as shown in Table 1.1. Similar conclusions were drawn from their comparisons of O₂ and CO from the same groups.

Results from Stankiewicz et al., 1993, also seemed to suggest the independence of kinetic energy release of the fragmentation channels on laser pulse risetime when they investigated the dissociative ionization of N₂ using 248 nm wavelength laser light and pulse durations of 1 to 4 ps. Schmidt et al., 1994, experimenting on Cl₂ came to a similar conclusion. Hatherly et al., 1994, however, looked more closely at
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the kinetic energy releases of I\(_2\) dissociatively ionizing using 750 nm wavelength laser light of 200 fs and 400 fs pulse durations. They found that there was indeed a dependence of kinetic energy releases with pulse risetime but that dependence was much less than was predicted by the field ionization Coulomb explosion model (Codling et al, 1987). An accurate experiment (Giles et al, 1995) was carried out using the technique of laser interferometry which allowed the modification of the pulse risetime without the alteration of any of the other laser parameters. The careful measurement of the kinetic energy releases of I\(_2\) led the authors to believe that, as suggested by Hatherly et al, 1994, there is a small dependence of kinetic energy release on the laser pulse risetime.

1.4 Bond Softening and Bond Hardening

Bond softening is an above threshold dissociation (ATD) process which occurs after an initial ionization of a molecule when further absorption of photon energy leads to dissociation. The kinetic energies of the fragment ions are typically much smaller than the kinetic energies of the fragment ions produced by Coulomb explosion processes. Bond softening, first postulated by Giusti-Suzor et al, 1990, predicted multiphoton absorptions occurring in the dissociation continuum of the product ion H\(_2^+\). In this model repulsive states are field-dressed, which is a term to describe the virtual absorption of \(n\)-photons by a molecule (where \(n \geq 1\)). This dressed state can be presented on a potential energy curve diagram, as shown in Figure 1.6, such that it crosses a bound molecular state. Due to the non-crossing rule the dressed states of the same parity do not cross and an avoided crossing ensues. When a state is dressed by a photon the parity of the state changes by (-1).

If the molecule is promoted to the g, \(n=0\) state it can dissociate via tunneling of the atomic fragment ion/neutral through the potential barrier lowered by the avoided crossing of the bound state and the dressed repulsive curve, as shown in Figure 1.6. Bond softening also occurs where the molecular ion is promoted to the g, \(n=2\) curve and tunnels adiabatically onto the u, \(n=3\) curve dressed with three photons. During dissociation some of the photons used in the dressing of the potential curves can be returned to the laser field via stimulated emission.
Figure 1.6: The avoided crossing of a bound state and a repulsive dressed molecular state, resulting in tunneling and low energy dissociation.

The modification of the potential curves results in a very small kinetic energy for the dissociated atomic fragment ions/neutrals for both of the bond softening processes described above, due to the fact that the energy difference between the asymptote of the repulsive curve and the height of the barrier formed by the avoided crossing of the bound and repulsive state is small.

The first experimental verification of this theoretical model was presented by Bucksbaum et al., 1990. Using 532 nm, 100 ps laser pulses on laser produced \( \text{H}_2^+ \) molecular ions the measured kinetic energies were compatible with bond softening. The process of production of the \( \text{H}_2^+ \) ion from the \( \text{H}_2 \) molecule occurs on the rising edge of the laser pulse and the bond softening dissociation occurs later within the same pulse. As in ATD they found that there were peaks in the proton spectrum separated by \( \hbar \omega/2 \) and as in ATD they interpreted this as a sharing of the photon energy by the neutral and ionic products of dissociated \( \text{H}_2^+ \). For higher laser intensities the avoided crossing gap opened up and they concluded that the lower kinetic energy fragments detected were due to lower vibrational states participating in the dissociation.
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![Figure 1.7: Intensity dependence of the proton spectra for 355 nm laser light. The lower spectra, A, collected with \( I = 5 \times 10^{13} \text{ W/cm}^2 \) and the upper spectra, B, with \( I = 1 \times 10^{14} \text{ W/cm}^2 \). The expected proton energies for the different unperturbed vibrational levels of the \( \text{H}_2^+ \) ground state are marked on the bottom of the figure. At the higher laser intensity the relative amount of protons coming from the dissociation of the ions in the lower vibrational levels increases (Zavriyev et al, 1990).](image)

Zavriyev et al, 1990, were also able to detect protons produced by the bond softening process and claimed to be able to distinguish protons liberated from different vibrational levels, as shown in Figure 1.7, for 355 nm laser light. Figure 1.8 shows how Zavriyev et al, 1990, explained that lower kinetic energy fragments were detected for higher laser intensity due to the unbinding of the lower vibrational levels with increasing laser intensity.

Giusti-Suzor and Mies, 1992, investigated theoretically the dissociation of \( \text{H}_2^+ \) from different vibrational states by solving the time dependent Schrodinger equation. They found that for vibrational levels less than \( v=4 \) the molecule dissociates at earlier and earlier times in the laser pulse for increasing vibrational level. Figure 1.9 shows that this is due to the crossing point of the bound and repulsive states that occur at this vibrational level of the bound state. The non-crossing gap widens with increasing intensity. However, they found that there was a reluctance for the molecule to dissociate in vibrational levels higher than \( v=4 \). They named this phenomenon bond hardening. Figure 1.9 shows a bond hardening process occurring for \( v=10 \) due to the intensity-modified upper curve c. The vibronic wave packet, originally in the vibrational level \( v=10 \), is trapped in the upper well produced by the avoided crossing between the bound \((g,n=0)\) and repulsive \((u,n=1)\) state. As the laser intensity decreases and the non-crossing gap narrows lower vibrational levels to \( v=4 \) will be trapped in this upper level.
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Figure 1.8: One photon crossing for 532 nm light. Solid lines show the unperturbed $1s\Phi_0$ state and the $2p\Phi_0$ state lowered by one photon. The component of the laser field parallel to the internuclear axis perturbs the states. As the laser polarization increases the gap between the states opens, and more vibrational states become unbound. (Zavriyev et al, 1990)

Figure 1.9: Field dressed $1s\Phi_0$ and $2p\Phi_0$ states of $H_2^+$. Curve a: $l = 5 \times 10^{14}$ W/cm$^2$, curve b: $l = 2.5 \times 10^{14}$ W/cm$^2$ and curve c: $l = 1 \times 10^{14}$ W/cm$^2$. $\gamma_1$ is the total kinetic energy for bond softening dissociation and $\gamma_0$ is the kinetic energy for the bond hardening dissociation (Giusti-Suzor and Mies, 1992).

A significant population could be trapped in these light induced vibrational bound states and is a possible mechanism for stabilization against dissociation, discussed in Section 1.6, since it means that the dissociation could be postponed to later in the laser pulse.
Zavriyev et al, 1993, continuing the work of Zavriyev et al, 1990, investigated the intense laser field dissociative ionization of H$_2^+$ and D$_2^+$ using 160 fs 769 nm laser light. They found structure within the kinetic energy spectra of the deuteron and the proton which they attributed to the vibrational structure of the ATD and population trapping (bond hardening). The paper describes the bond hardening process temporally through the pulse, as shown in Figure 1.10.

Figure 1.10: A possible population trapping scenario. During the second vibrational cycle the vibrational wave packet becomes trapped in the adiabatic well above the three-photon avoided crossing between the 1s$\sigma_g$ and 2p$\sigma_u$ states of the molecular ion. The fine lines show the 1s$\sigma_g$ ground state as well as the 2p$\sigma_u$ state shifted down by integer numbers of photons (Zavriyev et al, 1993).

At low intensities the vibrational wave packet is bound within the 1s$\sigma_g$ state modified by the avoided crossing of the 2p$\sigma_u$ state dressed with 1$\gamma\omega$. Within the pulse duration vibrations of the molecule are possible even as the laser intensity increases. When the intensity is high enough the 2p$\sigma_u$ dressed with 3$\gamma\omega$ forms an avoided crossing with the 1s$\sigma_g$ state and trapping of the vibrational wave packet occurs in the potential well created by the 2p$\sigma_u$-3$\gamma\omega$ repulsive curve and the 1s$\sigma_g$ bound state. At the peak of the pulse the ion ionizes for a second time from the trapped state. Zavriyev et al, 1993, concluded that this is the first experimental verification of light induced trapped states that are stable against dissociation but can be detected by the photoionization of the molecular ion.
Figure 1.11: The trapping of \( v=12 \) for \( \text{H}_2^+ \). The population is trapped in an adiabatic well formed by the avoided crossing (Giusti-Suzor et al, 1995).

Giusti-Suzor et al, 1995, continuing the theoretical interest in the processes of bond hardening and bond softening for different vibrational states shows how complicated the dissociation of \( \text{H}_2^+ \) is due to the number of possible processes there are, as shown in Figure 1.11. Wunderlich et al, 1996, theoretically investigated \( \text{Ar}_2^+ \) and found that increasing the laser frequency moves the avoided crossing to smaller internuclear distances. All of these discoveries show how dramatically the dynamics of dissociative ionization of molecules can be affected by the characteristics of the laser pulse.

1.5 Enhanced Ionization: Quantal and Classical Interpretations

For many years it has been known that the kinetic energy releases of the channels produced by intense laser field dissociative ionization were not equal to the Coulomb explosion energies for the molecule dissociating from the equilibrium separation, but were in fact much lower than expected (see for example Schmidt et al, 1994). Different reasons for this were suggested, for example the stepwise ionization of the molecules (references in Section 1.1) or that stretching of the internuclear bonds by centrifugal forces reduce the kinetic energies from those expected from the equilibrium internuclear distances (Cornaggia et al, 1994).
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However, these interpretations were unsatisfactory in explaining the evidence. The interpretation which fits most experimental data is that of enhanced ionization.

Enhanced ionization is the term to describe the increased ionization rate at a particular range of internuclear separations known as the critical range. The mechanism by which this occurs has been described by both quantal and classical models (see for example Seideman et al, 1995a, Bandrauk et al, 1995 and Posthumus et al, 1995). The first significant work on this subject was Codling et al, 1989, whose classical field ionization Coulomb explosion model predicted enhancements of ionization of diatomic molecules at particular internuclear distances and angular orientations of the molecular axis with the laser field direction. Figure 1.12c shows how the ionization rate is enhanced by ionization over the inner barrier of the diatomic molecule.

Figure 1.12: The field ionization of a diatomic molecule when the laser polarization direction is a) perpendicular and b) and c) parallel to the internuclear axis of the molecule. The difference between b) and c) is that in c) the molecule has expanded and the ionization energy of the localized electron has been Stark shifted.

Schmidt et al, 1994, explained the lower than expected kinetic energies of the fragment ions as due to ionization occurring at a specific critical internuclear distance. They noted that the ratio of the experimentally determined kinetic energies to the calculated Coulomb explosion kinetic energies from the equilibrium separation was dependent on the molecule under investigation and was almost independent of the laser characteristics. (see for example Normand et al, 1993, and Codling and Frasinski, 1993).

The first investigation of this phenomena was by Chelkowski and Bandrauk, 1995b. They point out that in a diatomic molecule the electron is free to move from one nucleus to another but finds it difficult to ionize. However, at larger internuclear
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separations the electron tunneling from one nucleus to another can gain sufficient kinetic energy in the laser field to overpass the lowest outer barrier and escape. This can only happen when the internal barrier (which increases with increasing R) is not too large. These two competing tendencies led them to the conclusion that for a specific electric field there must be a particular internuclear separation which maximized the ionization; the critical distance, \( R_c \), discussed in Section 1.7.

\[
\text{Figure 1.13: Ionization rates of } \text{Cl}_2^{5+} \text{ ion into } \text{Cl}^{6+} + \text{Cl}^{8+} \text{ as a function of internuclear distance for a range of laser intensities of 790 nm wavelength (Chelkowsk}\text{i and Bandrauk, 1995b).}
\]

This interpretation was the preliminary for a following quantal description. They solved the time dependent Schrodinger equation numerically for a 1D electron in a Coulomb field, and found that the critical distance hardly depends on the laser intensity, as shown in Figure 1.13, or the charge of the ion. Closely following this publication was that of Posthumus et al, 1995a, which classically modeled a diatomic system. They, too, found that the critical distance was independent of the charge state of the ion. Zuo and Bandrauk, 1995, solved the 3D time-dependant Schrodinger equation as a function of internuclear separation and found that the ionization rate exhibits a maximum at large R. Specifically, they found that there was an enhanced ionization rate from 5 au to 12 au for \( \text{H}_2^+ \) in \( 10^{14} \text{ W/cm}^2 \) at 1064 nm wavelength.

Seideman et al, 1995a, performed 1D calculations solving the Schrodinger equation on a generic diatomic \( \text{A}_2 \) and found that electron localization was pivotal to the theory of enhanced ionization. They justify using 1D calculations since the dissociation of diatomic molecules is 1D with the laser electric field direction. They explained that the localized electron in the lower potential well has less chance of ionization, but that localization in the upper well has a better chance of ionization due to tunneling of the trapped population through the internal barrier and into the
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continuum. All the charge states showed strongly enhanced ionization in the same internuclear region and that the envelope of the probabilities of ionization over the critical region was insensitive to the laser frequency.

![Figure 1.14](image)

**Figure 1.14:** (a) Ionization rate vs internuclear distance for $A_i^{3+}$ at $I = 9 \times 10^9$ W/cm² and $A_2^{5+}$ at $I = 1.2 \times 10^{14}$ W/cm² and (b) Ionization probability following the short pulse $I(t) = I \sin^2 (\pi t/T)$ with $T=30$ fs. Full squares represent the numerical probability for $A_i^{3+}$ at $I = 9 \times 10^9$ W/cm²; circles represent the numerical probability for $A_2^{3+}$ at $I = 9 \times 10^9$ W/cm²; open squares represent the modified ADK theory for $A_i^{3+}$; triangles numerical represent the numerical probability for $A_2^{5+}$ at $I = 9 \times 10^9$ W/cm² and diamonds represent the numerical probability for $A_2^{5+}$ at $I = 1.3 \times 10^{14}$ W/cm² (Seideman et al, 1995a).

Seideman et al, 1995a, suggested that several electrons are stripped away from the molecule until the first repulsive charge state ($A_2^{2+}$ or $A_2^{3+}$) is reached, after which it dissociates to the critical distance, $R_\text{c}$. At this internuclear separation the ionization rate is strongly peaked for several successive ionization stages. The intensity needed to reach the repulsive state $A_2^{2+}$ near equilibrium is sufficient to rapidly ionize several more electrons in the critical region, producing a series of highly charged states. They, too, found that $R_\text{c}$ hardly depended on laser intensity or charge state of the ion, as shown in Figure 1.14. Table 1.2 shows the results of their calculations of the critical distances for several molecules compared with experimental results from Schmidt et al, 1994.
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Table 1.2: The calculated values of the critical distance, \( R_c \), from Seideman et al, 1995a, compared to the experimental results of critical distance from Schmidt et al, 1994.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Calculated ( R_c )</th>
<th>Experimental ( R_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2 )</td>
<td>2.87</td>
<td>2.34</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>3.1</td>
<td>2.62</td>
</tr>
<tr>
<td>( H_2 )</td>
<td>3.1</td>
<td>2.75</td>
</tr>
<tr>
<td>( Cl_2 )</td>
<td>3.3</td>
<td>2.8</td>
</tr>
<tr>
<td>( I_2 )</td>
<td>3.9</td>
<td>3.6</td>
</tr>
</tbody>
</table>

This work was extended by Seideman et al, 1996, in which triatomic molecules were considered. They compared the enhanced ionization envelope for a symmetric and an asymmetric stretch of the generic triatomic molecule, \( A_3 \), within a 20 fs laser pulse. In both cases the ionization rate increased by 3 to 5 orders of magnitude within 1 Bohr, peaked at \( R_c \) and then rapidly decreased, as shown in Figure 1.15. They found that for both symmetric stretch and asymmetric stretch the inner barriers play no significant role and thus the ionization is atom-like.

![Figure 1.15](image)

**Figure 1.15:** The ionization rate of a triatomic molecular ion as a function of the internuclear separations (a) \( A_3^{5+} \rightarrow A_3^{6+} + e^- \) and (b) \( A_3^{6+} \rightarrow A_3^{7+} + e^- \) for an intensity of \( 10^{14} \) W/cm\(^2\) and laser wavelength of 1130 nm (Seideman et al, 1996).
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1.6 Laser Induced Stabilization

The concept of laser induced stabilization was introduced by Fedorov et al., 1975, Yuan and George, 1978 and Bandrauk and Sink, 1981. Laser induced stabilization has been used to describe two different processes; stabilization against ionization and stabilization against dissociation. At the end of the pulse, or at a specific intensity, the stabilization is lost and the molecule can dissociatively ionize. (Bandrauk and McCann, 1989).

McCann et al., 1992 investigated how stabilization could account for an unexpected dip in the dissociation probability with intensity by solving the time independent Schrodinger equation. Figure 1.16 shows the dissociation probabilities of Li₂ calculated by McCann et al., 1992. They suggested that the dip in the dissociation probability of the upper curve is due to stabilization of the molecule.

![Figure 1.16: The ‘dip’ in the dissociation probability, interpreted as stabilization by McCann et al., 1992.](image)

Frasinski et al., 1994, investigated CO₂ with the aid of covariance mapping and concluded that stabilization may be used to explain the results. They suggested that the electrons were collectively promoted to highly excited states, but that dissociative ionization was not immediate. The laser electric field was thought to stabilize these states but that as the field magnitude increased the stabilization mechanism was lost and the electrons were ejected followed by dissociation of the molecule.
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Ivanov, 1994, provided some further insight into the possible practical reasons for stabilization against ionization. He explained that stabilization, or suppression of ionization, is due to the coupling of the ground state of the molecule with a Rydberg state with which it is in resonance. When the electron is excited into the continuum it can do three things a) emit a photon b) continue in its motion in the Kepler orbit or c) absorb a photon and ionize; stabilization occurs as b). He states that the stability of the wavepacket is due to the coupling of many Rydberg states to the same initial states below, which give rise to an efficient destructive interference of transitions to the continuum. Geltman, 1994, solved the time dependent Schrödinger equation for a variety of laser frequencies and for a variety of processes including multiphoton ionization, tunnel ionization and over the barrier ionization. He concluded that the ionization probability approached one as the intensity increased and no signs of ionization suppression or stabilization of the bound state were seen in that limit.

Schmidt et al, 1994, summized that if stabilization of molecules was occurring then the process of PDI could not occur since the initial dissociation and ionization would take place at the end of the pulse. They carried out an experiment of dissociative ionization of Cl₂ by a 2 ps duration laser pulse in which they specifically looked for evidence of PDI and, in keeping with their hypothesis, found none. In a complimentary experiment Schmidt et al, 1995, were able to show that subsequent ionization of fragment ions would occur if the mechanism of stabilization were removed. The experiment was a double pulse experiment, as shown in Figure 1.17. Within the envelope of a 2 ps pulse the first pulse dissociatively ionized the molecule and the second pulse produced further ionization of the fragment ions. Hence, they had apparently reproduced the conditions required for dissociative ionization and PDI but had avoided the stabilization mechanism. Since no secondary ions had been found in the experiment which used the 2 ps laser pulse (Schmidt et al, 1994) they deduced that it was stabilization that had prevented it.

Schmidt et al, 1995, suggested that the light-bound states postulated by Bandrauk, 1994, provide the mechanism for stabilization. Here it is postulated that stabilization is caused by transitions between charge transfer or charge resonance states. Schmidt et al, 1994, note that the kinetic energies of the fragment ions are independent of the laser pulse duration and laser intensity and are solely dependent on the molecule. However, it is hard to reconcile that light induced bound states are independent of the intensity of the light.
Posthumus et al., 1995a suggested that the molecule relaxed to $R_c$ where it stabilizes against dissociation and subsequently ionizes with little or no inter-ion separation for different ionization stages. This work is a classical over the barrier model extended from the field ionization Coulomb explosion model (Codling et al., 1987) involving simple calculations of molecular potential wells perturbed by the laser field and the modification of the ionization potentials due to the laser induced Stark shifts. The outermost electron can move freely in a double well, but as the ions move apart the inner barrier rises and at $R_c$ it starts to impede the movement of the electron such that it can no longer follow the field and the system makes a transition to a non-dissociative, or stabilized state.

Ivanov et al., 1996, extending their previous work on the possibility of laser induced suppression, or stabilization (Ivanov, 1994) performed numerical and analytical calculations for the generic $A_2^{3+}$ molecular ion in which all of the potential surfaces are unstable in zero field. Thus, any stability must be due to the applied field. Classically one stabilizes a diatomic molecular system by forcing the electron to spend most of the time half way between the two nuclei where the single charge compensates for the Coulomb repulsion. They found that the unstable molecule could be stabilized near $R_{eq}=2\alpha$ (where $\alpha$ is the amplitude of the oscillation of the electron) for very high laser frequencies. For lower laser frequencies the opposite was found to be the case and deviations from the repulsive Coulomb potential were suppressed. As the calculations involved only one electron the authors concluded
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that it is possible that molecular stabilization could be due to some collective multi-electron dynamics.

1.7 Classical and Quasi-classical Models of Dissociative Ionization Involving the Critical Distance

The origin of these classical models of ionization, used for intense laser field dissociative ionization, is the classical over the barrier field ionization Coulomb explosion model (Codling et al, 1987). The crucial point is that at a particular internuclear separation the least bound electron is able to escape from the rising well over the inner barrier into the continuum. The term for this particular internuclear separation, the critical distance, $R_c$, was introduced into the literature by Zuo et al, 1993.

Chelkowski and Bandrauk, 1995b used 1D time dependent Schrödinger equation calculations to explain that, for an internuclear separation less than $R_c$, the electron is free to move from one nucleus to another, through the inner barrier, but ionization is difficult because of the high ionization potential. However, at $R_c$ the electron, moving from one nucleus to another, gains enough kinetic energy in the laser electric field to overcome the lowest outer barrier and escape. At $R_c$ the electron has the most favorable conditions to move through the external and internal barriers, as explained in Section 1.6. Posthumus et al, 1995b subsequently developed a purely classical model to explain the relevance of the critical distance. The central point of the model was that the molecule relaxes to $R_c$ where it stabilizes and ionizes with little or no internuclear change of $R_c$ for different ionization stages. This classical model focused on the outer electron and combined all the other electrons and nuclei into two point-like atomic ions. The striking difference between the description of the events given by Chelkowski and Bandrauk, 1995b and Posthumus et al, 1995a, is that the latter involves the concept of electron localization.
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Figure 1.18: Ionization of I₂ for low and higher laser intensity and showing the effect of increasing the internuclear separation to \( R_c \).

As the molecule moves apart the inner barrier starts to rise such that at \( R_c \) the electron can no longer follow the field and is confined, or localized, in a single potential well, as shown in Figure 1.18b. The applied field causes the electron energy level of the lower potential well (shown on the RHS of Figure 1.18b) to decrease by \( \mu E \) and increase by the same amount in the upper potential well (shown on the LHS of Figure 1.18b). The increase in energy level due to electron localization at \( R_c \) results in ionization. The potential wells of the diatomic were calculated from Equation 1.3 (Posthumus et al., 1995b).

\[
U = -\frac{Q_1}{x + \frac{R}{2}} - \frac{Q_2}{x - \frac{R}{2}} - \varepsilon x
\]

Equation 1.3

where \( Q = Q_1 + Q_2 \) is the sum of the atomic core charges, \( x \) is the axial position, \( R \) is the internuclear separation and \( \varepsilon \) is the laser electric field. The average energy level, \( E_L \), of the outer electron in this symmetric, double well can be approximated by Equation 1.4 (Posthumus et al., 1995b).

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

Equation 1.4
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where $E_1$ and $E_2$ are the known ionization potentials of the atomic ions. The model predicts the fragmentation energies of the different ionization channels. Figure 1.19 shows a comparison of experimental kinetic energies from various research groups and the kinetic energies predicted by this model.

Posthumus *et al*, 1996, continued their earlier work on the refined field ionization Coulomb explosion model, and used the modified model to predict the classical appearance intensities for diatomic molecules as a function of internuclear separation. Figure 1.20a shows how the modification of the potential wells, due to the laser field, makes ionization unlikely at small internuclear separations ($< R_c$), very likely at $R_c$ and unlikely again at larger internuclear separations ($> R_c$). Figure 1.20b shows how the ionization was modeled following the intensity progression of the laser pulse. The point within the pulse at which the ionization occurs can be determined.

![Figure 1.19](image_url)

**Figure 1.19:** Kinetic energy releases for $N_2$, $O_2$, $CO$, $Cl_2$, $I_2$ and $CO_2$ (Posthumus *et al*, 1995b).
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Figure 1.20: Double well potentials for $I_2^+$ at three different internuclear separations in a strong electric field, illustrating the calculation of the classical appearance intensity of $I'_+ + I'$. (Intensities in W/cm$^2$). $I_{app}$ is the appearance intensity for that ionization stage.

Figure 1.21 shows how the internuclear separation required for dissociative ionization into various channels varies with laser intensity. The dotted lines on Figure 1.21 are the trajectories of the laser pulses of different intensities and pulse durations. The highest charge state produced by that laser pulse is found from the graph by observing the maximum charge state (solid line) crossed by the dotted line. Using this model it is also possible to predict the point in the laser pulse at which ionization takes place. Ionization was shown to occur in rapid succession on the rising edge of the pulse, contradicting the theory of stabilization which requires ionization to occur on the falling edge of the laser pulse.

Figure 1.21: Classical appearance intensities of the $(Q_1, Q_2)$ fragmentation channel of $I_2$ (solid curves) and classical trajectories (dashed curves) Posthumus et al, 1996.
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1.8 Molecular Alignment and Bending in the Intense Laser Field

Codling et al, 1987, found that when HI was exposed to an intense laser field the fragment ions were detected moving parallel to the laser polarization direction. Codling et al, 1989, proposed a model which accounted for this observation. The model, known as the field ionization Coulomb explosion model, explained in Section 1.1, suggested that the population of molecules that were oriented parallel to the field had a higher propensity to ionize than those oriented perpendicular to the field since the barriers of the potential wells of the molecules aligned parallel to the field were lowered by the electric field of the laser while the barriers of the potential wells of the molecules aligned perpendicular to the field were essentially unaffected by the field and, thus, remained stable against ionization, as shown in Figure 1.22. The authors believed that the ionization was guided by an orientational propensity rather than alignment of the molecules by the laser field.

![Figure 1.22](image)

Figure 1.22: Field ionization of a diatomic molecule, showing the effects of increasing the internuclear separation and orientation of the molecular axis by the laser field on the ionization. All figures are shown with a laser E field of 3.2 V/Å and a total charge of q=2. In (a), (b) and (c) the laser E field is parallel to the molecular axis and in (d), (e) and (f) it is perpendicular (Codling and Frasinski, 1993).
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Hatherly et al, 1990, investigated the angular distribution of dissociating ions and used the notation of $\cos^\theta$ to describe the distribution of the ions detected with respect to the electric field direction. Hatherly et al, 1990 investigated CO interacting with 750 nm laser light of 200 fs and 400 fs pulse durations. They found that the higher the channel order the tighter the fragment ion distribution ($C^+ + O^+$; $n=6 \pm 2$: $C^2+ + O^*$; $n=8 \pm 2$: $C^2+ + O^{3+}$; $n=10 \pm 2$).

Normand et al, 1992, performed a double pulse experiment which contested the idea that it was the original orientation of the molecule with respect to the laser field direction that determined whether or not it ionized. The two pulses were separated by 800 ps with the laser polarization direction in the first pulse perpendicular to the second. The duration between the two pulses was chosen such that there was not enough time for the random molecular motion at room temperature to refill the focal volume of the laser beam with molecules. The authors proposed two hypotheses. The first was that the leading pulse would only interact, as proposed by Codling et al, 1989, with molecules where the molecular axis was parallel with the laser polarization direction and the second pulse would do likewise. Due to the randomness of the orientation of the molecules the ratios of the fragment ions detected would be nearly equal. The second was that the laser was reorienting the molecules before ionizing them, and so the first laser pulse would interact with the whole population of molecules; reorient and ionize them. The second laser pulse would not have a population left to ionize and few ions would be detected. The latter was the conclusion of the paper, and the results are shown in Figure 1.23. The same paper also showed the first direct angular measurements of ions from the dissociation, as shown in Figure 1.24.

Strickland et al, 1992, investigating I$_2$ found that I$_{3+}$ was more peaked (tighter angular distribution) than I$_{5+}$ which was in agreement with Hatherly et al, 1990, in that higher charge state angular distributions are peaked more along the laser polarization direction. They suggested that the large polarizability of the molecule provided the mechanism for the gain in angular momentum required to produce these distributions.
**Figure 1.23:** Ion TOF spectra of CO produced by (a) the first laser pulse alone, the polarization of which was perpendicular to TOF axis, (b) the second laser pulse alone, the polarization of which was parallel to TOF axis and (c) the first and second laser pulses successively fired with a time delay of 800 ps between them. (Normand et al, 1992).

**Figure 1.24:** Angular distributions of the main fragments observed in the dissociative ionization of CO where a) shows the angular distribution of the carbon ions and b) the angular distribution of the oxygen ions (Normand et al, 1992).
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Luk et al, 1992, investigated the linear triatomic N₂O molecule constituting different isotopes of nitrogen (¹⁴N in the terminal position and ¹⁵N in the central position) such that they could determine how the molecule was dissociatively ionizing in the laser field. They found that unlike in the case of high energy ion impact the atom in the terminal position is more likely to be ionized to a higher state than the central atom. They suggested that the reason for this difference is partly due to the reorientation of the molecules, in the intense laser field. They suggested that the laser first aligns the molecule parallel to the laser field direction and then dissociatively ionizes the molecule along its axis.

Dietrich et al, 1993, questioned the hypothesis that alignment of the molecules occurred and was followed by dissociative ionization, which had been advocated by Normand et al, 1992, Luk et al, 1992, and others, and put forward an alternative explanation for their results. The molecule under investigation, I₂, was chosen because of its high inertia such that its natural rotation is insignificant for the duration of the laser pulse (446 ps/J where J is the rotational quantum number). Although the molecular ions cannot translate or rotate on the time scale of the laser pulse (1 ps), it was suggested that they can gain enough momentum to deflect the trajectories of the fragments significantly. They put forward two hypotheses. The first was that the molecules oriented perpendicular to the laser polarization direction are not ionized or at least that there is a smaller probability of ionization. The second was that ionization is independent of the angle θ between the molecular axis and the laser polarization direction, but that the fragment ions are deflected towards the direction of the laser electric field vector during the dissociation.

![Figure 1.25: Angular distribution for dissociative ionization of I₂. Shown is the ion yield of the fragmentation channel I₂⁺ → I⁺ + I as a function of angle between the laser polarization direction and the TOF axis. The acceptance angle is 28°. The solid line is the fit S = cos⁴θ. (Dietrich et al, 1993).](image)
Dietrich et al, 1993, concluded that since natural rotation can not be the cause of molecular reorientation it must be due to the induced dipole moment. This moment creates a torque on the molecule which aligns it in the field. The rotation due to the dipole moment need not be complete by the end of the pulse. The induced torque may simply set the dissociating molecules on curved trajectories. They calculated that for an 80 fs laser pulse the final angles of the molecular fragment ion trajectories were determined 10 ps after the maximum of the pulse. The major difference, then, between this theory and that of Normand et al, 1992, is that Normand assumed that the reorientation occurred within the laser pulse and prior to ionization while Dietrich et al, 1993, suggested that the ionization must occur within the laser pulse but reorientation could continue after it.

That strong electric fields can hybridize low rotational states of polar molecules was suggested by Friedrich, 1995. He suggested that this hybridization results in pendular states in which the molecular axis is confined to librate over a limited angular range about the field direction during the pulse. This work was furthered in Friedrich and Herschbach, 1996, when they applied the theory specifically to intense laser field experiments. They postulated that the states could be driven by either a permanent dipole moment (in the case of a polar molecule) or an induced dipole moment (in the case of either a polar or non-polar molecule). Kumar et al, 1996, measured the angular distributions of \( \text{O}^+ \) from CO\(_2\) and \( \text{S}^+ \) from CS\(_2\) (both linear molecules) in a 35 ps laser field and found ion distributions that showed that the ions were initially moving along the field polarization direction. These distributions, called lobes, were centred around 0° and 180° and are shown on Figure 1.26. They also observed some structure on these lobes such that there appeared to be more \( \text{O}^+ \) ions detected at approximately 30° than 0° for CO\(_2\) and more \( \text{S}^+ \) ions detected at approximately 25° than 0° for CS\(_2\). They interpreted these results as direct evidence of the pendular states.

The effect of the alignment of the molecule on the geometry has also been investigated. Comaggia et al, 1994, suggested that the widths of the oxygen and carbon peaks obtained from the dissociative ionization of CO\(_2\) showed that the molecule is not always in the linear configuration when it dissociates. They found evidence of bending of the molecule around an average linear structure. The bending was tentatively assigned to bending vibrations arising from the violent laser
induced alignment of the molecule along the laser polarization direction before Coulomb explosion.

Figure 1.26: Angular distributions of (a) O* from CO$_2$ and (b) S* from CS$_2$ arising from the interaction of the parent molecule with 532 nm laser light of 35 ps pulse duration. The polarization axis of the incident radiation is horizontal (0°) (Kumar et al, 1996).

Cornaggia, 1995, continued this work, but this time he compared more complex molecules, C$_3$H$_4$ and C$_3$H$_6$, the structures of which are shown in Figure 1.27. Comparing a simulated covariance map with his experimentally produced covariance map he was able to deduce that the parent molecule was both bent and stretched by the laser electric field prior to dissociative ionization. The molecule was stretched from 0.5 R$_e$ to 1.5 R$_e$ and the bend angles were in the range of 140° to 220°.

Figure 1.27: The molecular structure of (a) C$_3$H$_6$ and (b) C$_3$H$_4$ under zero field conditions, and (c) C$_3$H$_4$ bent by the laser field.
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Cornaggia, 1996b, in an effort to better quantify the bending of the molecule returned to investigate the simpler linear triatomic \( \text{CO}_2 \) and saw the bending and stretching in the laser field that he had previously seen with the larger hydrocarbons. Analyzing both the 1D TOF spectra and covariance map he found that the oxygen and carbon peaks were comparable in width which he interpreted as an indication of bending motions of the molecule, since a stiff exploding molecule would produce narrower carbon peaks. The angles \( \alpha \) and \( \theta \), shown in Figure 1.28, were used to characterize the orientation \( (\theta) \) and bending \( (\alpha) \), of the \( \text{CO}_2 \) molecule.

![Figure 1.28: The angles characterizing the orientation (\( \theta \)) and bending (\( \alpha \)) of \( \text{CO}_2 \) (Cornaggia, 1996b).](image)

Table 1.3: The angles characterizing the orientation (\( \theta \)) and bending (\( \alpha \)) of \( \text{CO}_2 \) (Cornaggia, 1996b). (\( \theta_{1/2} \) and \( \alpha_{1/2} \) are half \( \theta \) and \( \alpha \))

<table>
<thead>
<tr>
<th>Channel</th>
<th>( \theta_{1/2} )</th>
<th>( \alpha_{1/2} )</th>
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<tbody>
<tr>
<td>(111)</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>(121)</td>
<td>20</td>
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<td>(221)</td>
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</tr>
<tr>
<td>(222)</td>
<td>15</td>
<td>20</td>
</tr>
</tbody>
</table>

To explain his results Cornaggia suggested that the Coulomb interaction between the displaced bound or freed electrons and the nuclei produce additional bending and stretching forces with an overall torque applied on the nuclear structure. Cornaggia et al., 1996a, investigating \( \text{SO}_2 \), which has a permanent bend angle of \( 119.5^\circ \) found that the molecule was unbent to \( 180^\circ \) by the laser field.

The effects of the laser on the alignment and bending of molecules is not yet fully understood. In fact the exact mechanism for the alignment is not known although
possible suggestions have been made, as mentioned in this section. How can the molecule bend and stretch in the field? The geometry of the molecule, or even the electronic structure, does not appear to have a straightforward relationship with the way the molecule fragments in the laser field and the question of how these geometric modifications occur remains unanswered.

1.9 Presented work

In order to help clarify some of the problems in understanding the molecular interactions with intense laser fields raised in this chapter a programme of experimental investigation was undertaken:

1. Investigations of N$_2$O dissociation channels in a 35 ps and 60 fs laser field and kinetic energy determinations of the ionic fragments (Chapter 5).

2. Investigations of CO$_2$ angular alignment and orientation in the laser field (Chapter 6).

3. Investigations of CO$_2$ excitation from a vibrationally excited state - orientation and alignment (Chapter 6).

4. Investigation of the fragmentation patterns of SF$_6$ (Chapter 7).

This chapter has shown that diatomic molecules have been extensively studied in this field and their behaviour is well understood. However, triatomic molecules have been largely ignored to date, with a few notable exceptions. The Dissociative ionization of diatomic molecules in intense laser fields has been successfully modeled by the refined field ionization Coulomb explosion model (Posthumus et al, 1996). It is attempted in this thesis to provide more experimental data, of the fragmentation patterns of the two triatomic molecules, the internuclear separations of the constituent ions at Coulomb explosion and, in the case of CO$_2$, the trajectories of the fragmenting ions such that theoretical investigations of triatomic molecules may be provoked. Sulphur hexafluoride has been studied in the programme for similar reasons. Larger molecules have been studied by various
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research teams, for example Vijayalakshmi et al, 1997, studied CCl$_4$, CHCl$_3$, and CH$_2$Cl$_2$ and Comaggia et al, 1992, studied longer chain hydrocarbons C$_2$H$_4$ and C$_2$H$_2$. However, the octahedral geometry of SF$_6$ means that it is possible to analyze this molecule in a similar way to the triatomic molecules investigated in this thesis such that its polyatomic nature can be investigated.
Chapter 2: The Apparatus

2.0 Introduction

In this chapter a description of the design and operation of the apparatus, including a description of the vacuum system, the time of flight mass spectrometer, residual gas analyser and the gas inlet system is given. Also included is a discussion of the technique required to determine the initial kinetic energies of ions from a time of flight spectrum.

2.1 The Vacuum System

The main considerations in the design and construction of the vacuum chamber were to:

i) Allow the easy transportation of the vacuum chamber.
ii) Enable reflection focusing of femtosecond pulses.
iii) House the optics required for the focusing of picosecond pulses.
iv) Produce a sufficiently low residual pressure as to be insignificant compared to the very low gas pressures used in this work.
v) House the time of flight mass spectrometer.
2.1.1 The Vacuum Chamber

A diagrammatic representation of the apparatus arrangement is given in Figure 2.1. The vacuum chamber was made with as small an internal volume as possible, while still allowing reasonable adjustment of the apparatus within. The object was to produce a background pressure of < 1 \times 10^{-9} \text{ mbar}. This was achieved not only by minimising the surface area to be pumped and the length of the vacuum seals required, but also by careful selection of the materials used in the manufacture of the apparatus positioned within the chamber. Although PTFE is UHV compatible it is porous and out-gases solvent for several days after it has been cleaned. Ceramic was the preferred insulating material, since it out-gases less than PTFE. All the chamber ports were sealed with OFHC copper gaskets, except the laser entrance and exit windows which were sealed with annealed copper gaskets.

![Diagram of the vacuum chamber system.](image)

Figure 2.1: The vacuum chamber system.

The chamber was in the form of a four way symmetrical cross, as shown in Figure 2.1, with four main flanges (diameter 200mm): two vertical, S1 and S2, and two horizontal, T and B. The laser exit and entrance ports, E1W and E2W, (diameter 67mm) were on opposite sides of the vertices of the cross. The internal apparatus was mounted from the top flange and could be lowered into the chamber. The
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electronic feed-throughs for the time of flight mass spectrometer and detector, PS, were mounted on this flange as was the gas leak valve, LV, (VG Model : MD6). The Residual Gas Analyser, RGA, (Model : 160-121-001, discussed in section 2.3) and ionization gauge, IG, ( VG Model : VIG 22) were mounted on flange S1, as well as the feed-through, HL, for the internal heating bulb (Osram Xenophot HLX 150W). The remaining flange, S2, was an access flange upon which were mounted the gas heating filament and thermocouple feed-throughs.

The Balzer's turbo pump (Model : TPU 450 H) was mounted on the bottom flange, B. The system was backed with a Balzer's diaphragm pump (Model : MD4) for an oil free pumping system. Both pumps were controlled by a Balzer's electronic drive unit (Model: TCP 380).

To initiate the pumping of the chamber from atmospheric pressure the turbo pump electronic drive unit was turned on. This started the turbo pump and backing diaphragm pump simultaneously. When the pumps were used to pump the chamber from atmospheric pressure the current driving the turbo blades was 7.15 A initially. A real-time value of the current was shown on the display panel on the front of the electronic drive unit. As the pressure in the chamber decreased so too did the current. When the pressure was lower than 1 x 10\(^5\) mbars the current driving the turbo blades, was 1.1 A, with a blade rotation frequency of 760 Hz.

The blades in the turbo pump rotate faster in lower pressures, as there is less resistance to their movement, and thus, if the frequency was still not at the optimum value, within the specified time duration, a gross leak is indicated. An automatic electronic trip, to shut down the pumping system, was employed such that if the optimum operation frequency of the rotating blades was not achieved within forty minutes the turbo and diaphragm pumps were turned off. When the system is shut down, either by the electronic trip or by manually switching off the electronic drive unit, the diaphragm pump stops pumping immediately. Power loss to the turbo pump, however, results in a decrease in the blade rotation frequency and a decline in the pumping speed until pumping eventually terminates.

The blade frequency decreases very slowly, initially, as the blades are in vacuum and there is very little resistance to their movement. An argon gas supply is attached to the magnetic vent valve. Once the rotation speed has decreased to 185 Hz, which
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takes approximately 10 minutes, the magnetic venting valve (Model: TSF 012) opens automatically and an inert argon atmosphere fills the chamber, minimising the exposure of the channel plates (see Section 2.8) to oxygen and water, which reduces their efficiency. The rotation rate decreases very rapidly as the argon atmosphere hinders the turbo blade’s movement. With an initial chamber pressure of $5 \times 10^{-8}$ mbar, and an argon gas head pressure of 10 kPa, atmospheric pressure within the chamber is achieved in approximately 15 minutes after the shutdown of the electronic drive control unit.

The ionization gauge measures the ambient pressure in the chamber. The ionization gauge control unit (Model: IGC 27) trip facility was used to terminate the mains voltage to all the power units supplying the apparatus within the chamber if the pressure rose above $1 \times 10^{-5}$ mbar. The trip was only employed when the experiment was running; otherwise it was overridden.

When the turbo pump blade frequency reached the working value of 760 Hz, the ionization control unit was initiated in order that any pressure change could be monitored. Once the pressure in the chamber fell to below $1 \times 10^{-5}$ mbar the residual gas analyser could be employed.

2.1.2 Interior of the Vacuum Chamber

The gas flow into the chamber was controlled by a Vacuum Generators leak valve, LV, (Model: MD6). On the vacuum side of the valve PTFE tubing was attached to the nozzle on the inside of the conflat flange and the other end of the tubing attached to the gas beam needle situated near the interaction region, as shown in Figure 2.2, in a crossed beam formation. The chamber also housed a channel plate detector, described in Section 2.8, laser beam focusing optics for both picosecond and femtosecond pulses discussed in Sections 3.2.4 and 3.3.9, and a time of flight mass spectrometer, discussed in Section 2.5. The arrangement of this apparatus is shown schematically in Figure 2.2.
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The bottom extraction plate of the detector, upon which the femtosecond focusing optic is mounted, can be rotated and the picosecond focusing lenses are removable such that either the picosecond or femtosecond focusing optics can be used.

2.2 Gas Line

The apparatus arrangement used to transport the test gas into the extraction region consists of two parts: The external and internal gas lines, or the gas transport apparatus outside and inside the vacuum chamber respectively.

2.2.1 The External Gas Line

The gas line arrangement is shown in Figure 2.3. It was not designed with ultra-high vacuum considerations in mind. The minimum pressure which could be reached with this system was $5 \times 10^{-3}$ mbar, as measured with a pirani gauge (Vacuum Generators Model: M6A) and displayed on a Vacuum Generators control Unit (Model: IGC 27).
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The gas line was constructed with Edward’s aluminium vacuum piping (internal diameter: 25 mm), as well as copper piping, (internal diameter: 12 mm) and copper tubing (internal diameter: 2 mm), all sealed with viton o-rings.

The gas was transported down the copper piping, as shown in Figure 2.3, to the leak valve, LV, (VG Model: MD6) which was mounted on a specially adapted conflat flange.

![Diagram of the external gas line]

Figure 2.3: The external gas line

The gas line was pumped by a two stage Edward’s Rotary pump (Model: IEC 34). A sorption trap was included in the arrangement and was kept under vacuum at all times. In the event of the Rotary pump being switched off the diaphragm valve was closed and the venting valve opened to atmosphere immediately the pump was deactivated. This procedure prevented back-streaming of oil into the gas line. Before the rotary pump was switched on again, the activated alumina spheres (diameter 2 - 5 mm) were heated to 300 °C, for a duration of four hours, to reactivate them before being returned to the sorption trap.
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2.2.2 The Internal Gas Line

A nozzle was welded to the inside of the conflat flange upon which the leak valve, LV, was mounted. PTFE tubing (internal diameter of 4mm) was attached to the nozzle and the other end attached to a hypodermic needle positioned, as shown in Figure 2.4, within the extraction region. The hypodermic needle was used to inject the test gas into the interaction region but was not designed to produce a gas beam.

Figure 2.4: Gas injection apparatus

Figure 2.4 also shows a coil of Kanthal wire and a thermocouple wrapped around the hypodermic needle. The function of these two components is explained in Section 2.6.

2.3 Residual Gas Analyser

The residual gas analyser was a useful commercially produced product that determined the mass to charge ratios of contaminants in the vacuum chamber. The leak testing facility was used to pinpoint the position of leaks between the chamber and conflat flanges. The residual gas analyser (Leda-Mass Model: 160 121 001) is comprised of:
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* Twin filament analyser with dual (Faraday cup and electron multiplier) detector and 1-100 amu mass range capability
* UHV ion source fitted with thoriated iridium filaments
* Control unit (Model:100D) with RS232C computer interface, integral micro-processor and front panel LED filament, detector and communications status indication
* RGA for windows software package to operate in the windows environment

The analyser can be explained in three separate parts by virtue of their function. The ion source is located at the top of the analyser and its function is to take a representative sample of the molecules and atoms from the vacuum chamber, convert them into ions and inject them into the quadrupole filter. This filter is the centre section of the analyser. Its function is to take the ion beam generated in the ion source and separate the various ions by their mass to charge (m/q) ratio and transmit the singly selected m/q to the collector. The collector converts the filtered ion beam produced by the quadrupole filter into a small electrical current which is passed to the electronics for amplification and subsequent display on the computer screen.

Thus, the RGA's function is to collect and determine the mass to charge ratio of ions produced from gas (background or otherwise) in the vacuum chamber, and display data. This data could then be utilised in several ways. The primary use of the RGA was to provide a graph showing the various partial pressures of the ions produced from the molecular and atomic contents of the vacuum chamber and, thus, enable the determination of the vacuum contaminants. For comparison, the RGA software contains a library of the mass/charge fragment ions it would produce from 25 common vacuum contaminants. Another useful facility of this unit is that it provides a total pressure reading, which is a useful comparison with the ionization gauge pressure value.

2.4 Leak Testing and Chamber Baking Procedure

A directional helium source is sprayed over the seals of the chamber and the RGA's helium detection level is set to a range of the required sensitivity, depending on the magnitude of the leak. The computer produces an audible sound, varying in pitch, to
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give an indication of the amount of helium the analyser, situated within the vacuum chamber, is detecting. A real-time graph of helium levels versus time is displayed on the PC screen.

When the chamber's gross leaks have been detected and eliminated the system is left to pump, usually overnight, until the pressure reduces to a constant value. Thermotrace glass fibre-covered heating coils were attached around the chamber to heat the outside of the system and a 150 W Osram Xenophot bulb (HLX) positioned inside the chamber provided internal baking. There was also a heating element around the turbo pump, since the final pressure of the chamber is also a function of the cleanliness of the pump. The chamber and turbo pump were covered with a fibreglass 'tent' to reduce heat loss. The chamber was baked at a temperature of 200 °C. The pressure rose from, typically, $1 \times 10^7$ mbar to $8 \times 10^6$ mbar, over several hours. The temperature was maintained until the pressure had dropped to approximately $1 \times 10^6$ mbar, which usually took a few days. Care was taken to reduce the temperature gradually, after baking, to avoid breakage of the laser entrance and exit windows. The minimum pressure before baking was $1 \times 10^7$ mbar, and after baking $4.6 \times 10^{10}$ mbar. Figure 2.5 shows the RGA results for when the chamber was (a) recently pumped from atmosphere and (b) after the baking procedure was completed.

Figure 2.5a, shows the residual gas spectrum in the chamber pumped down from atmospheric pressure. The spectrum shows that there was a significant amount of air and water in the vacuum chamber prior to baking. The amounts of carbon dioxide and hydrogen levels are a greater proportion than are in air. This is because these two substances are difficult to pump out of the chamber as they adhere to the chamber walls more successfully than the other contaminants. Figure 2.5b, showing the residual gas spectrum in the chamber after the baking and pumping, indicates that the total residual chamber pressure has decreased dramatically and, thus, the baking procedure was successful.
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Figure 2.5: The RGA results for when the chamber was (a) recently pumped from atmosphere and (b) after the baking procedure was completed.

2.5 Technique of Time of Flight Mass Spectrometry

The term mass spectrometer applies to any device that has the ability to separate gaseous ions according to their mass to charge ratio. In the time of flight mass spectrometer a bunch of ions is accelerated and projected through a field free space towards a detector. The flight time for each ion is a function of its mass to charge ratio, so the detector receives a series of separate ion bunches. A mass to charge
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spectrum is obtained by recording the detector current versus time. Figure 2.6 shows a time of flight spectrum of hydrogen. The parent ions, $\text{H}_2^+$, have been separated in time from the lighter fragment ions due to the greater effect of the extraction field on the lighter ions.

![Time of flight spectrum of hydrogen](image)

**Figure 2.6:** A time of flight spectrum of hydrogen recorded with the laser polarization direction parallel to the TOF axis. The extraction field was 10 V/cm, the gas pressure was $1 \times 10^{-7}$ mbar and the laser intensity was $3 \times 10^{15}$ W/cm$^2$. The different fragmentation processes have produced protons with differing energy. The peaks labelled (a) are ions due to the Coulomb explosion dissociative ionization process, (b) are the ions due to the 2-photon ATD process and (c) are ions due to the 1-photon ATD process.

Certain intrinsic complications arise in time of flight experiments and the design of the spectrometer can minimise the effects of these problems. The information deduced from the time of flight spectra is limited by the:

i) Mass to charge resolution of the ions.

ii) Energy resolution of the ions.

iii) Angular resolution of the ions.

The Wiley and McLaren type spectrometer (Wiley and McLaren, 1953), which is used in the present work, includes three regions through which the ion must pass: The extraction, acceleration and field-free drift regions (see Figure 2.11).
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The laser beam crosses the mid-point of the extraction region perpendicular to the detector axis, as shown in Figure 2.7. A balanced, static field is applied across this region and, thus, the ionising beam traverses the zero volt equipotential.

![Diagram of laser beam and extraction plates](image)

**Figure 2.7:** The extraction region of the time of flight mass spectrometer.

The ions are extracted by the applied static electric field across the extraction region (CD in Figure 2.11) and accelerated through the acceleration region (DE in Figure 2.11) and into the drift tube (F in Figure 2.11). The difference between the flight times for the ions with different mass to charge ratios is increased by the passage of the ions down the relatively long distance of the field free region. The detector is positioned after the field-free region at the exit of the spectrometer.

In isolating the problem of mass resolution one can see that the initial ion formation position is important. Since the target source is diffuse within the interaction region it is the radial thickness of the ionising beam, $\Delta R$, which determines the spectrometer image thickness. This variation in initial ion position results in a spread of flight times for particles of the same mass, charge and initial velocity. The inclusion of the accelerating region into the spectrometer design enables the focusing of ions with the same mass, charge and velocity components to arrive at the detector at the same time whatever their formation position across $\Delta R$ (Wiley and McLaren, 1953).

A further complication in these types of experiments is that ions begin their flight, not at rest, but with dissociative and/or thermal motion. This results in the ions reaching the detector at a range of flight times, both before and after the zero energy ion would reach the detector.
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(a) Top extraction plate
(b) Bottom extraction plate

Figure 2.8: The time of flight peaks when (a) the initial ion motion is parallel to the detector axis and (b) the initial ion motion is perpendicular to the detector axis.

Figure 2.8 shows how the direction of the energetic fragments determines the peak shapes of the spectrum. When the ions initially move perpendicular to the detector axis a single peak is observed, as shown in Figure 2.8b. However, when the fragmenting ions initially move parallel to the detector axis the forward ion arrives at the detector first, at T2, followed later, at T3, by the backward moving ion which is decelerated before its direction is reversed and is accelerated towards the detector.

Determination of the fragmentation energies of the ions can be found from the time of flight spectrum peak using Equation 2.1.

\[ K_E = \frac{1}{8} \left( \frac{q^2}{m} \right) E^2 \Delta t^2 \]  
Equation 2.1

where \( K_E \) is the initial kinetic energy of the ion (J), \( q \) and \( m \) are the electronic charge and mass respectively (C and kg), \( E \) is the electric field across the extraction region (V/m) and \( \Delta t \) is the time difference between the ions moving towards the detector (forward moving ions) and ions moving away from the detector (backward moving ions) (s). The derivation of Equation 2.1 is given in Appendix 2. The Equation 2.1 can be used to determine the kinetic energy distribution of the ions of specified mass and
charge, simply by determining the $\Delta t$ values for the entire range of energies of the ions contributing to the time of flight peaks as shown in Figure 2.9.

$\Delta t =$ time difference between the forward moving and backward moving ion
$KE =$ kinetic energy calculated using Equation 2.1
$KE_1 =$ calculated using $\Delta t_1$
$KE_2 =$ calculated using $\Delta t_2$
$KE_3 =$ calculated using $\Delta t_3$

**Figure 2.9:** The kinetic energy distribution of the time of flight peaks for ions dissociating along the time of flight axis.

The difference in the flight time of the ions in the forward and backward ion peaks is a result of the component of velocity of the ions along the time of flight axis. The component of velocity of the ions along this axis is as a result of both the ion's initial kinetic energy and direction. Thus Equation 2.1 is useful in producing kinetic energy values if the dissociation of the ions is confined to a small range of angles, or to put it another way, if the dissociation is anisotropic along the TOF axis.

Figure 2.10 illustrates two situations where in both cases the kinetic energy of the ions are the same value, but their initial direction differs. This results in the component of velocity of the ions along the time of flight axis being different. Thus, the time of arrival of the ions at the detector, and hence the kinetic energies as determined from Equation 2.1, will not be the same.

When the ion fragmentation is isotropic, meaning that the fragmentation is equally probable in all directions, double structure time of flight peaks may still be seen. In this case the double peak structure arises because the angular acceptance of the detector for that particular ion is less than 180° such that the molecules dissociating...
perpendicular to the detector axis are outside the acceptance angle and, therefore, remain undetected.

![Diagram](image)

**Figure 2.10:** Depicting the importance of the acceptance angle in the time of flight spectrometer. Showing (a) a dissociating ion fragmenting along the detector axis and (b) at an angle to the detector axis

An ion produced in the extraction region is both extracted and accelerated down the time of flight mass spectrometer. In order for it to be detected the time taken for the ion to escape the limiting width of the detector must be shorter than the time taken for the ion to travel the distance from its point of origin to the detector. The limiting width is the maximum distance the ion can move perpendicularly to the TOF axis before it can no longer be detected. Under the apparatus arrangement for the present work the width of the channel plate, shown in Figure 2.11, was the limiting width. Thus, it is obvious that the acceptance angle is not only dependent on the mass, charge and the extraction field, but also the ion's initial kinetic energy. A visual basic program was written to determine the angular acceptance for an ion of specified mass, charge and energy for given extraction and acceleration fields and drift potential. The program code is given in Appendix 3.
2.5.1 Design of the Time of Flight Mass Spectrometer

The spectrometer is a Wiley and McLaren type time of flight mass spectrometer, which includes extraction, acceleration and field free drift regions.

![Diagram of the spectrometer](image)

Figure 2.11: Time of flight mass spectrometer.

All the elements are constructed from stainless steel, insulated from one another with ceramic spacers and mounted as shown in Figure 2.11. The whole electrode structure is mounted within an earthed housing to protect the charged particles from stray electric fields. The grids, with an optical transmission of 90%, were fixed to the electrodes with colloidal graphite (DAG). It was important to keep the grids as flat as possible to avoid distortions in the applied fields. The drift tube was one piece of stainless steel tube (internal diameter 25 mm), which was fixed in position by a ceramic collar and located using the spectrometer mounting.

The extraction potential plates were designed to minimise the equipotential distortions and produce a uniform electric field across the extraction region. This was achieved by using smooth surface electrodes, maximising the electrode radii and designing the
region such that it consisted of two parallel, horizontal plates. The height of the extraction region was limited by the size of the optical elements for focusing the femtosecond beam. To produce a well-resolved spectrum it is necessary to make the flight tube as long as possible. The total length of the spectrometer axis was limited by the size of the vacuum chamber to 110 mm.

2.5.2 Testing the Time of Flight Mass Spectrometer

In order to confirm that the TOF mass spectrometer was operating correctly two tests were conducted on the system:

i) Comparison of the times of arrival of the parent and fragment ions with a computer simulation of the ion flight times from their point of origin to the detector.

The total flight times of ions moving toward and away from the detector, through the extraction and acceleration fields and the drift region, were calculated using Newton's equations of motion. The total flight time is defined as the time taken for the ion to move from its point of origin to the detector.

A visual basic program was written to calculate the time of flight of an ion of specified mass and charge and initial kinetic energy of 0 eV, in each region of the spectrometer. It also provided a value for the time of flight of an ion moving initially toward and away from the detector under chosen potential conditions. Figure 2.12 shows a comparison of the total flight times for N$_2$O parent and fragment ions with an initial velocity of 0 eV parallel to the TOF axis deduced from the simulation and from the experimental results. The gradient of the experimental and calculated relationship is the same. Each experimental TOF differs from the calculated value by 280 ns. This is due to the counter in the MCS (see Section 2.9) being triggered 280 ns before the light enters the vacuum chamber. This is unaccounted for in the simulation.

ii) Confirming the correct calibration of the time of flight mass spectrometer by observing the effect of changing the extraction field.
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The relationship between the ions time of flight and its charge and mass is shown in Equation 2.2. The derivation, from Newton's equations of motion, is given in Appendix 4.

\[ T_i = \sqrt{\frac{m}{q}} \left[ \frac{d_e}{E_e} + \frac{\sqrt{d_e E_e + d_a E_a + K_e q}}{E_a} - \frac{\sqrt{d_e d_a E_a + K_e q}}{2 \sqrt{d_e E_e + d_a E_a + K_e q}} \right] \]

- Equation 2.2

where \( T_i \) is the total time of flight of the ion from the point of origin to the detector, \( d_e \) is the distance from the ion point of origin to the exit of the extraction field, \( d_a \) is the distance across the acceleration field, \( d_d \) is the drift region length, \( E_e \) is the extraction field, \( E_a \) is the acceleration field, \( K_e \) is the initial kinetic energy of the ion and \( m \) and \( q \) are the mass and charge of the ion respectively.

Figure 2.12: A comparison of the total flight times for N\(_2\)O parent and fragment ions with an initial velocity of zero parallel to the TOF axis deduced from the simulation and from the experimental results. The offset is due to an electronic delay.

The gradient of a \( \frac{m}{q} \) versus \( T_i \) graph is linear if the initial kinetic energy of the ion (calculated from the velocity parallel to the TOF axis) is 0 eV. The linear gradient is dependant on the extraction and acceleration fields. Thus, the linearity of such a graph can be assured if the peak determination of the zero positions is correct. Figure 2.13 shows how the zero positions for some of the fragment ions vary with extraction field.
Chapter 2

Figure 2.13: A calibration graph for the fragment ions of N₂O for 4 different extraction fields.

2.6 Vibrational Excitation of Molecules

Collisions between a molecule and a surface can result in the transfer of energy from one to the other, resulting in the excitation of the molecule to which the energy is transferred. Equation 2.3 can be used to determine the temperature of the molecules within the heated surface, such that their mean thermal energy, \( E \), is enough to result in excitation of the test gas molecules into vibrationally excited states, \( E_v (\nu > 0) \).

\[
E = \frac{3}{2} kT
\]

Equation 2.3

where \( k \) is the Boltzmann constant and \( T \) is the temperature of the surface.

The method used to heat the gas molecules into an excited state was to introduce them into the extraction region via a hypodermic needle around which a coil of Kanthal heating wire was wrapped, as shown in Figure 2.4.

The temperature of the gas was monitored by wrapping a thermocouple around the tip of the hypodermic needle that is situated 10 mm from the laser focus. The thermocouple consisted of copper and constantan 32-gauge wire. The calibration of the thermocouple was carried out by measuring the voltages, using a Keithly auto-ranging multimeter (Model: 175A), for several temperatures.
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Table 2.1: The relevant details of the Kanthal heating wire.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max continuous operating temp</td>
<td>1673 K</td>
</tr>
<tr>
<td>Nominal composition</td>
<td>Cr (22%) Al (5.8%) Fe (72.2%)</td>
</tr>
<tr>
<td>Electrical resistivity at 20°C</td>
<td>1.45 Ω mm² m⁻¹</td>
</tr>
<tr>
<td>Melting point</td>
<td>1773 K</td>
</tr>
<tr>
<td>Coeff. of thermal expansion at 200°C</td>
<td>14 x 10⁻⁶ K⁻¹</td>
</tr>
</tbody>
</table>

The thermocouple was placed in a container of boiling water that was allowed to cool, to obtain more data points for the calibration. The temperature of the water was measured using a Digitron thermometer (Model: 1758-K) and compared to the thermocouple voltage readings. For the highest temperature (148 °C) the thermocouple and the Digitron thermometer was placed on the filament of an electric fire. Figure 2.14 shows the results for the calibration.

\[
\text{Temperature (°C) = Voltage (mV) - 0.744 - 0.44}
\]

![Temperature calibration graph](image)

Figure 2.14: Temperature calibration for the thermocouple voltage readings.

2.7 TOF Mass Spectrometer Acceptance Angle Determination

When carrying out direct angular measurement experiments the angular resolution of the apparatus is limited by the angular acceptance of an ion of a particular energy. The angular resolution of the experiment was also limited by the magnitude of the fields in the extraction, acceleration and drift regions of the spectrometer. A visual basic program was written to determine the angular acceptance of the spectrometer.
for an ion of a specific energy moving towards and away from the detector when the potentials on the elements of the spectrometer were specified. The code for this program is given in Appendix 3.

To achieve a very small acceptance angle for ions reaching the detector the potentials on the spectrometer elements were set at a high value (500 V/cm extraction field). Spectra were recorded for a range of laser polarization directions. In this way the relative number of ions moving initially along a particular trajectory, within the angular error set by the angular acceptance of the apparatus, could be found. A small acceptance angle allowed the detection of ions only within that angle resulting in better angular resolution of the final angular distribution spectra. The peak kinetic energies of the ions were determined as described in Section 2.5 and using this value the angular acceptance for each ion could be calculated using the visual basic program. This method is limited in that if a TOF peak is produced by many dissociation channels, and a distribution results, (see, for example, the dissociative ionization of N₂O in a picosecond laser field in Section 5.1) the peak energy of the distribution will result in an incorrect determination of the angular acceptance of that ion, but if the peaks are well defined (see, for example, the dissociative ionization of N₂O in a femtosecond laser field in Section 5.2.1) the angular acceptance values are more accurate.

Figure 2.15: (a) Shows that the geometry of the extraction region means that the forward moving ion (red line) can escape from the region at a bigger angle with respect to the TOF axis than the backward moving ion (blue line) and (b) shows the acceptance angles of the TOF mass spectrometer for forward and backward moving N⁺ ions.
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The acceptance angles for the forward and backward moving ions of a particular kinetic energy are slightly different due to the geometry of the TOF mass spectrometer extraction region, as shown in Figure 2.15a. Figure 2.15b shows the calculated acceptance angles of the TOF mass spectrometer for a forward and backward moving N⁺ ion. Figure 2.16 shows how the acceptance angles of the TOF mass spectrometer for forward moving N⁺ and N₂⁺ vary for different initial kinetic energies.

![Figure 2.16: The acceptance angles for the TOF mass spectrometer found from the visual basic program given in Appendix 3 for forward moving N⁺ and N₂⁺ ions.](image)

2.8 Detector and Circuit

Two multi-channel plates used in parallel form the active element of the detector. The chevron channels, which are at 13° through the detector, are set such that the channels of the two plates are in the opposite direction to each other, as shown in Figure 2.17. A ring electrode is positioned in electrical contact either side of the multi-channel plate. The operating voltage drop across each multi-channel plate was varied from 1.2 - 1.5 kV depending on the age of the multi-channel plate and the length of time it has been exposed to atmosphere. The typical detection channel plate efficiencies for positive ions and electrons provided by the manufacturer are given in Figure 2.18. The potentials dropped across the plates were provided by a resistor chain, which included a current protection circuit.
Grid 1, located in front of the first channel plate, MCP1, is positioned to repel any secondary electrons ejected from the front of MCP1 towards the drift tube. This is achieved by applying a voltage of more than 200 Volts more negative than the potential on the front of MCP1 to it. However, the positive ions passing through Grid 2, have sufficient energy to not be hindered by the opposing field. The output from the channel plate detector is taken via a screened coaxial cable to a fast risetime (< 1 ns) preamplifier (VT 120A), with a gain of 200, and then to the multi-channel scalar detection system. The signal pulses were negative pulses of 5 ns pulse width.
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2.9 Multi-Channel Scalar

The multi-channel scalar, MCS (Model: T814 Turbo-MCS™) is a product commercially produced by EG & G Ortec. The major features of the hardware are given below:

- Minimum dwell time per channel of 5 ns
- Maximum number of channels of 16,384
- Signal input rate of 150 MHz
- Zero dead time between channels

The MCS required a negative NIM pulse to trigger the scan and in the experiments described in Chapters 5, 6 and 7 this was taken from a synchronizing output signal from the nanosecond Nd-YAG laser for the femtosecond experiments and from a synchronizing output signal from the picosecond Nd-YAG laser in the picosecond experiments.

2.10 Summary

This chapter has included a description of the vacuum system, the gas inlet system, the Residual Gas Analyser (RGA) and the time of flight mass spectrometer. The detector circuit and counting hardware have been described. Also included was a discussion of the techniques required to determine the initial kinetic energy of an ion from a time of flight spectrum.
Chapter 3: The Picosecond and Femtosecond Laser Systems

3.0 Introduction

The 35 picosecond laser pulses required for the work presented in Chapter 5 were produced by a Nd-YAG laser consisting of a resonator cavity, translation optics, amplifier rod and a frequency doubling crystal. The system required to produce the 55 fs pulses used in the experiments presented in Chapters 5, 6 and 7 was more complicated. A Ti-Sapphire laser produced 50 fs pulses. This laser was pumped by an argon ion laser. The pulses were stretched and then amplified using a dye amplifier pumped by a nanosecond Nd-YAG laser and finally compressed to 55 fs. Both systems are described in this chapter as well as the procedures to align the beams correctly in the extraction region. The setting up procedure for the picosecond laser is also described.
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3.1 Picosecond Laser (Model: YG 501-C-20)

This pulsed solid state laser, a schematic of which is shown in Figure 3.1, produces picosecond pulses of wavelength 1064 nm, which are frequency doubled to 532 nm.

![Schematic of the Nd-YAG picosecond laser.](image)

<table>
<thead>
<tr>
<th>DC</th>
<th>= Dye cell</th>
<th>CC3</th>
<th>= Concave lens</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOM</td>
<td>= Acousto optic modulator</td>
<td>CV3</td>
<td>= Convex lens</td>
</tr>
<tr>
<td>PP</td>
<td>= Prism pair</td>
<td>M3</td>
<td>= Mirror</td>
</tr>
<tr>
<td>CV1</td>
<td>= Convex lens</td>
<td>M4</td>
<td>= Mirror</td>
</tr>
<tr>
<td>I1</td>
<td>= Iris</td>
<td>A2</td>
<td>= Amplifier unit</td>
</tr>
<tr>
<td>A1</td>
<td>= Amplifier unit</td>
<td>QWP1</td>
<td>= Quarter wave plate</td>
</tr>
<tr>
<td>CC1</td>
<td>= Concave lens</td>
<td>BD1</td>
<td>= Beam dump</td>
</tr>
<tr>
<td>E</td>
<td>= Flat etalon</td>
<td>BD2</td>
<td>= Beam dump</td>
</tr>
<tr>
<td>M1</td>
<td>= Mirror</td>
<td>P2</td>
<td>= Thin film polarizer</td>
</tr>
<tr>
<td>M2</td>
<td>= Mirror</td>
<td>P3</td>
<td>= Thin film polarizer</td>
</tr>
<tr>
<td>CC2</td>
<td>= Concave lens</td>
<td>HWP3</td>
<td>= Half wave plate</td>
</tr>
<tr>
<td>CV2</td>
<td>= Convex lens</td>
<td>KDP</td>
<td>= Frequency doubling crystal</td>
</tr>
<tr>
<td>P1</td>
<td>= Thin film polarizer</td>
<td>DM1</td>
<td>= Dichroic mirror</td>
</tr>
<tr>
<td>HWP1</td>
<td>= Halfwave plate</td>
<td>DM2</td>
<td>= Dichroic mirror</td>
</tr>
<tr>
<td>PC</td>
<td>= Pockels cell</td>
<td>DM3</td>
<td>= Dichroic mirror</td>
</tr>
<tr>
<td>GTP</td>
<td>= Glan-Thompson prism</td>
<td>PS</td>
<td>= Pulse selector</td>
</tr>
<tr>
<td>I2</td>
<td>= Iris</td>
<td>5%M</td>
<td>= 5% reflecting mirror</td>
</tr>
<tr>
<td>HWP2</td>
<td>= Half wave plate</td>
<td>DP</td>
<td>= Dove prism</td>
</tr>
</tbody>
</table>

*Figure 3.1: Schematic of the Nd-YAG picosecond laser.*
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The lasing takes place in an oscillator cavity, within which is the solid state laser medium, yttrium-aluminium-garnet (Y₃Al₅O₁₂) doped with neodymium ions (Nd³⁺). The Nd³⁺ are randomly distributed throughout the lattice at sites normally occupied by yttrium ions. It is the neodymium ions that provide the energy levels for the lasing and pumping. The function of the Y₃Al₅O₁₂, known as the host material, is to provide an electrostatic crystal field that results in the removal of the degeneracy of the Nd³⁺ energy levels, producing a four level system. Figure 3.2 shows the energy level schematic.

Various levels above the ⁴F₃/₂ are pumped by two xenon flashlamps contained within A1 on Figure 3.1. The ions in the lattice then relax by non-radiative decay to the metastable ⁴F₃/₂ energy level, which is the upper level for the 1.06 μm laser transition.

Table 3.1: Summary table of the output characteristics of the picosecond laser.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Output power</td>
<td>0.6 +/- 0.1 W</td>
</tr>
<tr>
<td>Energy per pulse</td>
<td>30 mJ</td>
</tr>
<tr>
<td>Pulse length</td>
<td>35 ps</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>20 Hz</td>
</tr>
<tr>
<td>Wavelength</td>
<td>532 nm</td>
</tr>
<tr>
<td>Beam divergence</td>
<td>1 mrad</td>
</tr>
</tbody>
</table>

Figure 3.2: Simplified energy level diagram for the neodymium ion in YAG showing the principal laser transitions.
**Chapter 3**

### 3.1.1 Mode Locking System in the Nd-YAG Laser

The Nd-YAG laser (Model: YG 501-C) produced mode locked pulses. Mode locking describes the process by which all the modes produced in the laser cavity are forced to maintain the same relative phase to each other. Removal of the transverse modes was achieved by positioning a pinhole, of 2.5 mm diameter, which is slightly bigger than the TEM\(_{00}\) mode diameter, within the cavity, as shown in Figure 3.3. The mode locking of the longitudinal modes is more difficult and is achieved by both active and passive techniques.

![Diagram](image)

**Figure 3.3:** Schematic of the Nd-YAG cavity optics showing the position of the acousto-optic modulator (AOM), the mode locking dye cell (DC) and the pinhole.

Active mode locking involves the use of an electro-optic or magneto-optic device to dump the modes and only allowing a few modes to oscillate within the cavity. Passive techniques do not involve electrical devices and rely on chemical interactions with light.

The acousto-optic modulator, shown in Figure 3.3 as the AOM, was the electronic switch used to achieve some active mode locking of the longitudinal modes. The AOM contains a piezo-electric crystal the refractive index of which changes when an acoustic wave passes through it. The medium's refractive index changes periodically within a wavelength, \(\Lambda\), equal to that of the acoustic wave, effectively producing a grating. As the refractivity of the medium changes the paths of the light
traversing the medium tend to bend into regions of compression of the acoustic wave. Only light that has undergone constructive interference will emerge from the other side of the crystal. This can only occur when the light waves are in phase with each other, which is the definition of mode locked light. The acousto-optic modulator, AOM (Model: MLE-6A) produced acoustic waves with a frequency of 70.15 MHz.

The passive longitudinal mode locking is accomplished using a dye the absorption of which decreases with increasing irradiance. Materials exhibiting this behaviour are called saturable absorbers. A dye is chosen which has an absorption band at the lasing transition frequency. Initially, at low light levels, the dye is opaque owing to the large number of unexcited molecules that can absorb light. As the irradiance increases, however, more and more of the excited states are populated until eventually all of them are filled so that the dye becomes transparent, or bleached. The laser medium emits spontaneous radiation that gives rise to incoherent fluctuations in the energy density within the cavity. Some of these fluctuations, which can be of short duration, may be amplified by the laser medium and grow in irradiance to such an extent that the peak part of the fluctuation is transmitted by the saturable absorber with little attenuation. The low parts of the fluctuation however are much more strongly attenuated and thus a high power pulse can grow within the cavity providing the dye can recover in a time short compared with the duration of the pulse. Because of the non-linear behaviour of the dye, the shortest and most intense pulses grow at the expense of the weaker ones. With careful adjustment of the concentration of the dye within the cavity an initial fluctuation may grow into a narrow pulse bouncing back and forth within the cavity producing a periodic train of mode locked pulses. A description of the preparation of the laser cavity for mode locking is given in Section 3.3.2.

3.1.2 Cavity Optics

As well as the dye cell/end mirror, DC, acousto-optic modulator, AOM, and pinhole, I1, which are mode locking devices, shown in Figure 3.3, the laser cavity also includes a convex, CV1, and a concave lens, CC1, a prism pair, PP, and the cavity flashlamp unit, A1. The cavity flashlamp unit contained a Nd-YAG cylindrical rod (4 x 65 mm) which was the laser medium and a xenon flashlamp to pump the medium.
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The convex and concave lenses were positioned to expand the beam profile such that the pinhole could exclude the higher order transverse modes from the beam. The prism pair was used to adjust the path length of the beam in the cavity to maximize the energy by ensuring the maximum number of longitudinal modes were resonant. A Fabry-Perot étalon, $E$, acted as an end mirror at the cavity exit. There were several manual settings on the étalon that enabled the pulse length to be altered. However, the experiments in this thesis used only the shortest available pulse duration setting of 35 ps.

3.1.3 Amplification and Steering Optics

The beam, exiting the cavity, is then steered by mirrors $M_1$ and $M_2$ into a telescope, consisting of concave and convex lenses, $CC_2$ and $CV_2$, to increase the area of the beam profile. This was so that when the beam entered the Pockels cell, $PC$, the energy of the beam was distributed across the crystal surface, reducing the possibility of hot spots within the crystal. The Pockels cell is a fast switching device used to select a single pulse from the mode locked train for amplification.

A Pockels cell uses the electro-optic effect to switch the polarization of the laser beam by $90^\circ$. When an electric field is applied across the birefringent optical medium the distribution of the electrons within the medium is distorted such that the refractive index of the medium changes anisotropically. The result of the electro-optic effect is to introduce a new optic axis into naturally refracting crystals. Figure 3.4 shows the effect of the electro-optic modulator on the laser polarization in the Nd-YAG picosecond system.

The next optical component in the beam path, as shown in Figure 3.1, is a Glan-Taylor prism, $GTP$, which transmits horizontally polarized light and reflects vertically polarized light. When the light is vertically polarized it is reflected by the GTP into the pulse selector, $PS$, (Model: SPS 411) via the dove prism, $DP$, and the 5% reflector mirror, $5\%M$. The pulse selector unit contains a photodiode which, when triggered, sends a voltage pulse to the Pockels cell. There is a manual delay control for the delay adjustment of the time between the trigger and the pulse to the Pockels cell. In front of the photodiode there is a pocket containing white paper strips that act as a light intensity filter. Both the manual delay adjustment and light
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Intensity filter are used to ensure that the most intense mode in the mode locked train is selected. The Pockels cell remains activated for 10 ns after it has been triggered by the pulse selector. This is the time interval between pulses in the mode locked train.

![Diagram of polarization and beam paths](image)

**Figure 3.4. The effect of the Pockels cell on the polarization direction of the laser light**

When the Pockels cell is in operation the polarization of light is changed by 90° such that it becomes horizontally polarized and passes through the Glan-Taylor prism. Another telescope, shown in Figure 3.1 as CC3 and CV3, further increases the area of the beam profile, and hence reduces the probability of producing a hot spot in the amplifier rod and causing damage to the optic. The beam is then guided by a high reflectivity mirror, M3, onto a thin film dielectric polarizer, P2, and into the double pass amplifier rod, A2. (dimensions 7 x 115 mm). The dielectric polarizer, P2, is positioned before the rod so that the linearly polarized light became circularly polarized. Circularly polarized light interacts with more of the Nd-YAG lattice, increasing the amplification efficiency. The amplified light is then reflected back through the rod by a flat mirror, M4, and is amplified again. The beam then passed though the dielectric medium, QWP1, which linearly polarizes the light, and then through a half wave plate, HWP3, which changes the polarization such that it becomes vertically polarized light.
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The next optical element in the beam path is the second harmonic generator, SHG. It contains a potassium di-hydrogen phosphate crystal more frequently known as KDP. This can be removed from the beam path so that the laser output remained as 1064 nm wavelength light, but the picosecond laser experiments presented in Chapter 5 used only frequency doubled 532 nm laser light. Once the second harmonic is generated the beam encounters a set of dichroic mirrors, DM1 and DM2, which reflect 532 nm light and transmit 1064 nm effectively separating the profile positions of the two wavelengths. The light then passes out of the laser exit.

3.1.4 Picosecond Power Supplies

The electronic units for the picosecond laser are shown below in Figure 3.5. The control unit (Model: CU 401), located at the top most position in the electronics rack, generates the clock rates and initiates the charging up of the capacitor banks by means of a signal exchange with the power units under its control. It also provides the security interlock function for the entire laser system. The control unit initiates all the commands to the system.

The electronic unit situated below the CU 401 is the MD 502, the function of which is to count the flashes of the xenon lamps in the amplifier units and display the total number. The MD 502 contains the electronic units for the pulse selector and the acousto-optic modulator. There is a manual adjustment for the frequency of the acoustic waves in the acousto-optic modulator, but it is factory set.

Below the MD 502 is the PU 420 power supply for the oscillator flashlamps. The function of this unit is to provide a current source to charge the capacitor banks. In addition there is a 24 volt dc supply which provides a synchronization signal to the capacitor bank to trigger the oscillator flashlamps.

The time between the production of the 24 V synchronizing output signal and the capacitor flashlamp discharge can be adjusted by altering the setting on the delay dial. There is also a dial allowing the manual adjustment of the potential to the laser flashlamp heads.
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The electronic unit CB 420S unit contains the capacitor bank for the oscillator amplifier. This unit produces the high voltage short duration pulses required by the flashlamp unit, A1, in the laser cavity. Below the PU 420 is the PU 430 below the CB 420S is the CB 430S, both of which perform the same task for the A2 as the PU 420 and CB 420 do for the A1.

![Diagram](image)

**Figure 3.5:** Schematic of the arrangement of the electronic rack for the picosecond laser.

The unit which is in the lowest position in the electronic rack is the CG 403 or cooling group. The purpose of this unit is to water cool the flashlamps and rods in the amplification units A1 and A2. Cold de-ionized water from the reservoir in the CG 403 unit is pumped to the amplification units where it carries away the heat before passing back into the reservoir to be cooled before re-circulation. The reservoir contains coiled pipes through which cold tap water passes maintaining the reservoir water temperature at about 15 °C.
3.2 Setting Up and Maintenance of the Picosecond Nd-YAG Laser

The maintenance of the laser involves ensuring good optical alignment along the beam path and the adjustment of angles between the beam path and active axes within the AOM and KDP crystals. The power at various positions along the beam path must be monitored as well as the laser beam profile. Other procedures such as mode locking and pulse selection require adjustments of cavity path length, delay settings to the Pockels cell and various other parameters which are described in Sections 3.2.1 to 3.2.3.

3.2.1 Alignment of the Optical Components within the Laser Cavity

Realignment of the optics in the cavity was required in about six monthly intervals as a result of gradual movement of the optics due to vibration and temperature. The optics were kept clear of dust by maintaining as much of a dust free immediate environment as possible and inspecting the optics for dust regularly. When dust had landed on the optics it was carefully removed by lens tissue dipped in high purity methanol. Realignment was carried out when the laser was in the free running condition. Free-running of the laser is a term meaning that no longitudinal active or passive mode locking is taking place. When the beam profile at the exit of the cavity was circularly symmetric the optics were deemed to be satisfactorily aligned. The beam profile was captured by placing a piece of Kodak burn paper in a clear plastic bag, at the end of the cavity after the étalon, and opening the cavity for a couple of seconds. Care was taken to keep the burnt fragments of the paper from landing on the optics and damaging them. Figure 3.6 shows an expanded beam profile when alignment is satisfactory and when readjustment of the cavity optics is necessary.

![Profile of a well aligned beam](image1) ![Profile of a badly aligned beam](image2)

*Figure 3.6: A well-aligned and badly-aligned beam profile taken at the exit to the laser cavity.*
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The realignment of the cavity involved the adjustment of the angles of the dye cell end mirror and the path length-modifying prisms in the beam. The end mirror was the first to be adjusted. The beam was required to pass back and forth through the fixed pinhole such that all the TEM$_{00}$ modes oscillate within the cavity. The mirror in the dye cell, DC, was then adjusted to maximize the power at the laser cavity exit. The beam power was measured using a Scientech calorimeter (Model: AC 2501 H) and power meter (Model: H 310). The beam power could then be converted into energy per pulse by dividing by the laser repetition rate.

The realignment of the mirror in the dye cell, DC, will result in a circularly symmetric beam profile at the end of the laser cavity and the maximization of the energy at the cavity exit. A typical energy of 6.25 mJ is expected during free-running for a well aligned cavity. The power meter at the cavity exit is replaced with the photodiode and the free-running oscilloscope trace is observed, as shown in Figure 3.7. The prism pair orientation, and hence the path length of the laser beam in the cavity, is then adjusted in order to maximize the height of the photodiode voltage trace. This adjustment ensures that the maximum number of longitudinal modes is oscillating within the cavity. After the path length has been optimized, readjustment of the dye cell mirror may be necessary since the beam path in the laser cavity may have altered such that the beam profile is no longer circularly symmetric.

3.2.2 Adjustment of the Longitudinal Mode Locking Dye

The dye solution in the dye cell is kept continuously flowing so that the molecules which have been excited by the laser are moved out of the beam path and have time to de-excite before they are pumped back into the beam path once again. The introduction of the laser dye to the dye cell was carefully implemented, according to an approved safety procedure, since both the dye and the solvent are hazardous to good health. The dye concentrate solution was made up of crystals of dye (7mg of Kodak 9740) dissolved in solvent (50 ml of Chlorobenzene). The dye concentrate was kept refrigerated to prolong its lifetime, the duration of which depends on factors such as duration of laser usage, temperature and contamination of the solution. The mode locking active ingredient of the dye, C$_{40}$H$_{43}$ClO$_6$, breaks up due
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to photodissociation by sunlight over a period of time resulting in the need to replace the dye about every 2 to 4 weeks.

The procedure of changing the dye begins by replacing the pump reservoir containing the spent dye solution with pure solvent. The solvent is pumped through the dye cell system flushing through expired dye solution that may remain in the tubing. The process of reservoir exchange is repeated with another reservoir of 30 ml of pure solvent.

The power supplies to the xenon flashlamp in the laser head unit, A1, are then switched on commencing optical pumping of the lasing levels of the Nd-YAG laser medium and a photodiode was placed after the Fabry-Perot etalon, E. The photodiode is connected to the oscilloscope to monitor the light intensity. With the acousto-optic modulator, AOM, not operating and only solvent in the dye cell the laser is free-running and the laser beam is only transversely mode selected. Figure 3.7 shows the oscilloscope trace of the photodiode, placed at the cavity exit, when the laser is free-running.

![Figure 3.7: The photodiode trace of the laser cavity output in the free-running condition](image)

The vertical axis of all the oscilloscope traces in this section is arbitrary since the voltage output depends on the amount of light entering the photodiode and this can be changed by repositioning the angle of the photodiode unit. The trace is a smooth positive slope indicating that there is no longitudinal mode locking. The duration of the trace is the length of time that the flashlamp is producing each pulse of light.

Active longitudinal mode locking was then commenced by switching on the acousto-optic modulator, AOM. The function of the AOM, was to produce only a few mode-locked pulses with the mode locking completed by the mode locking dye. The
oscilloscope trace, given in Figure 3.8, shows the photodiode trace of the beam which has been transversely mode selected and partially longitudinally mode locked by the AOM. Each step, of approximately 5 μs duration, contains a mode-locked train on the rising edge.

**Figure 3.8:** The photodiode trace at the cavity exit with the beam transverse mode locked and actively longitudinally mode locked.

**Figure 3.9:** The longitudinally mode locked and transversely mode selected beam at the exit to the cavity, when the oscilloscope is on the 1MΩ termination setting.

Dye concentrate is added to the solvent in the pumping reservoir in 1ml doses and the oscilloscope trace of the photodiode output is monitored after each addition. As the dye concentration increased the number of mode locked trains decreased. The dye concentration is increased until there is only one mode locked train left, shown as a single step in Figure 3.9.

Once the passive and active mode locking has been achieved the laser must be checked to see under what conditions double pulsing will occur. Although the rod is water cooled, there is a temperature differential between the outer part of the rod and the core. If the differential is great enough the rod can act as a thermal lens due to the difference in refractive index of the laser medium over the cross section of the rod. The result can be that the focusing of the laser beam is such that two or more transverse modes oscillate within the cavity. Figure 3.10 shows an oscilloscope trace from the
photodiode at the exit of the laser cavity of double pulsing of the beam. The two peaks are due to two transverse modes oscillating in the laser cavity.

Figure 3.10: Double pulsing of the laser beam.

The temperature differential occurs not only when the laser has been running for a long period of time but also when the voltage to the flashlamps is increased. The difference between the normal operating voltage and that required for the production of double pulsing should be greater than 40 V according to the manufacturer’s specifications. If the voltage difference were less than 40 V then the energy of the beam must be decreased to prevent thermal lensing occurring after prolonged running of the laser. More dye concentrate should be added to the solvent so that more photons are absorbed and the beam energy decreased.

Under stable mode locked conditions, the energy per pulse of the beam at the exit of the well-aligned laser cavity should be 3.5 - 4 mJ. The laser manufacturer states that 4 mJ is the safe limit for the optics in the cavity. Any increase beyond this energy and there is a risk that the optic coatings will be damaged by the laser light. Figure 3.11 shows the photodiode trace of the mode locked train at the cavity exit and viewed on the oscilloscope with a 50 Ω terminator.
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![Figure 3.11](image1.png)

*Figure 3.11:* The oscilloscope trace of a mode locked train of pulses viewed with a 50Ω terminator.

### 3.2.3 Beam Alignment of the Non-Cavity Optics, Pulse Selection and Second Harmonic Generation in the Nd-YAG Picosecond Laser

Alignment of the optics through the etalon, E, to the laser exit depends primarily on the angles of the three mirrors, M2, M3 and M4.

![Figure 3.12](image2.png)

*Figure 3.12:* Schematic of the outer cavity components in the Nd-YAG laser. (The notation is as for Figure 3.1).
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The procedure of alignment is carried out with the power to the amplifier rod off. Thus, the beam profiles are very weak and any gross misalignment does not lead to damage of the optics. The alignment procedure begins by adjusting the angle of the first mirror in this section of the laser, M2 in Figure 3.12. In order to align M2 the beam profile in front of M3 is monitored (shown in Figure 3.12 as Pos.1). Since the beam profile has been expanded by two telescopes, CC2 and CV2, and CC3 and CV3 it is easier to observe aberrations in the beam profile. Once the gross misalignment has been eliminated by aligning M2, M3 can be adjusted while the beam profile in front of M4 is monitored (shown in Figure 3.12 as Pos.2). Careful examination of the diffraction rings within the profile caused by the beams' passage through the optics provides information about the degree of alignment. Care must be taken, though, since dust on the optics can also create diffraction rings resulting in misinterpretation of the reason for the shape of the beam profile. Once a satisfactory beam profile has been produced M4 can be aligned. The beam profile in front of QWP2 is monitored (shown in Figure 3.12 as Pos.3). The beam profile at the exit of the laser is observed and if the diffraction rings are not concentric, adjustment of M4 is necessary. It is always necessary to return to M2, M3 and M4 since the adjustment of the optics is an iterative procedure. Figure 3.13 shows the results of good and bad alignment of the laser optics.

![Well aligned profile beam](image1)

![Badly aligned profile beam](image2)

*Figure 3.13: Beam profiles of the 532 nm beam at the exit of the laser, (Position 4 on Figure 3.12), showing the result of good and bad alignment of the laser beam.*

Once the alignment of the beam is satisfactory selection of the mode from the mode locked train must be examined and if necessary adjusted. Adjustment is necessary if the pulse selector, PS, is not selecting the longitudinal mode in the mode locked train with the greatest amount of energy or if not all of the pulse is selected. Again it must be ensured that the pulse selection modification procedure is carried out with the power to the amplifier rod, A2, not switched on.
Figure 3.14: The mode locked train of pulses sampled at the 5% reflecting surface with (a) no mode selection (PS is off) and (b) one of the modes selected, ie removed, (PS is on).

Figure 3.14a shows the photodiode trace of 5% of the complete mode-locked train, taken from mirror 5%M, when the pulse selector is not operating. Figure 3.14b shows the photodiode trace, taken at the same position, with the most intense mode selected out of the complete train. Figure 3.15 shows a flow diagram of the pulse selection technique. The numbers 1 to 11 indicate the passage of the beam and electrical signal with respect to time.

Figure 3.15: Flow chart of the pulse selection method.
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1-3. When the cavity is open, and the pulse selector is off, the light passes through the pulse selector.

4. The vertically polarized light is reflected by the GTP into the pulse selector via the Dove prism.

5. When the light is intense enough to pass through the light intensity filter, at the front of the pulse selector, the photodiode, at the back of the pulse selector, is activated and the pulse selector sends a signal to activate the Pockels cell.

6. The Pockels cell operates for 10 ns duration (the length of one of the modes) and switches the light polarization by 90° to vertical.

7-8. The vertically polarized mode passes through the GTP.

9-10. After 10 ns the Pockels cell is switched off and the rest of the mode locked train passes through it with unchanged horizontal polarization.

11. The GTP reflects the remainder of the horizontally polarized mode locked train to the pulse selector via the Dove prism.

Result. The light observed at the 5% reflection mirror and after the GTP is shown in Figure 3.14b.

There are two ways to change which mode is selected. The first is to alter the amount of light entering the selector by adding or removing white paper from the front of the pulse selector entrance such that a different mode has the light intensity required to trigger the pulse selector. This is the gross adjustment in mode selection. There is also a more sensitive adjustment, and this is used to ensure that the whole mode is selected. The duration of the delay between the trigger of the photodiode and the Pockels cell being activated can be altered. The manual delay is a dial on the back of the pulse selector. The effect of the alterations of the delay can be monitored by observing the photodiode oscilloscope trace at the 5% mirror.
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The final stage in setting up the Nd-YAG laser entails tuning the angle of the KDP crystal to maximize the transmission of the 532 nm light. A dial on the KDP unit adjusts the angle between the crystal birefringence axis and the laser beam direction to maximize second harmonic generation. Typically, when 532 nm light production has been maximized and the dichroic mirrors have separated the 532 nm light from the residual 1064 nm light, the energy of the 532 nm light is 36 mJ and the energy of the 1064 nm light is 14 mJ. The unfocused 532 nm light beam diameter was 9 mm.

3.2.4 Optical Manipulation and Alignment of the Laser Beam into the Vacuum Chamber

The optics used outside the Nd-YAG laser exit performed four tasks. Firstly, to steer the beam into the experimental chamber. Secondly, to select a polarization angle of the laser light entering the chamber. Thirdly, to regulate the energy of the beam and hence the focused intensity inside the extraction region and, finally, to focus the beam to a very small diameter.

The height of the vacuum chamber was adjusted until the centre of the entrance window, EW1, was at the same vertical height as the laser exit. Using a spirit level the laser and vacuum chamber were adjusted so that both were parallel with the floor of the laboratory. Assuming the laser light is perpendicular to the laser optical bench then the light polarization direction will be parallel to the time of flight axis of the TOF mass spectrometer. The beam was steered into the chamber via three mirrors of 99.7% reflectance, M5, M6 and M7, (TecOptics F1004 150 000). They were arranged, as shown in Figure 3.18, such that the possibility of the beam reflecting back into the laser, and damaging it, was much reduced. Alignment of the beam was deemed to have been achieved when the beam was found to be in the centre of the vacuum chamber entrance window, EW1, and the exit window, EW2. The angles of the mirrors were adjusted so that the beam profile was distorted as little as possible as it was steered into the chamber. Comparisons of the beam profile at the laser exit and after each mirror were made to ensure this was the case. The focusing of the 532 nm laser beam was achieved using two vacuum compatible 50mm focal length lenses, L1 and L2. The first, placed before the interaction region, focused the laser beam to a spot, FP, and the second, placed
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the same distance along the beam line after the interaction region, recollimated the beam, as shown in Figure 3.16. The vacuum chamber entrance and exit windows, EW1 and EW2, were concentric with the focusing lenses, L1 and L2, and with the mid-point of the interaction region. This focusing technique produced a maximum focused intensity of $3.5 \times 10^{14}$ W/cm$^2$ for this laser.

![Diagram](image)

**Figure 3.16** The chamber optics for focusing of the picosecond laser beam.

The first polarizer, P4, was temporarily positioned after the laser exit, before M5 shown in Figure 3.18, and its angle adjusted such that the beam energy measured after the polarizer was maximized. The polarizer was now set so that only vertically polarized light could pass through it. The polarizer was then moved and positioned after the last beam steering mirror, M7. The beam energy both before and after the polarizer was measured to determine whether the laser light polarization direction had been altered by the beam steering mirrors, M5-7. A similar procedure was followed for a second polarizer, P5, in order to determine the active axes of the component. The angular setting of the half wave plates, HWP4 and HWP5, were determined by placing P4, HWP4 and P5 in the beam path after M7 respectively. The polarizers, P4 and P5, remained set such that they transmitted only vertically polarized light. The transmitted energy was measured with respect to the angular setting on the half wave plate and the angular setting on HWP4 was found which changed the polarization direction by 90°. The results of this investigation are shown in Figure 3.17. The procedure was repeated for HWP5. The components were then placed in the beam path, as shown in Figure 3.18.
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Figure 3.17: The transmitted power of the laser beam as it passes through P4, HWP4 and P5.

The optics, HWP4 and P5, placed one after the other acted as an energy selector, with HWP4 altering the polarization angle of the beam and P5 ensuring that only the vertical component of the beam passed through it. Together they altered the energy of the beam but not the polarization direction. The other half wave plate, HWP5, was placed in the beam path after P5. The function of HWP5 was to alter the laser light polarization direction. Once all the optics had been placed in position alignment of the beam through the chamber was rechecked.

Figure 3.18: The arrangement for the external optics used in picosecond experiments.
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3.3 Femtosecond Laser System

The femtosecond laser system, located at the Rutherford Appleton Laboratory, was a hybrid system. The constituent lasers are products of several companies. Figure 3.19 shows a block diagram of the layout of the system components.

Figure 3.19: Schematic of the femtosecond laser system

Table 3.2: Summary table of the output characteristics of the femtosecond laser system.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Output energy</td>
<td>100 μJ</td>
</tr>
<tr>
<td>Pulse length</td>
<td>50 fs</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Wavelength</td>
<td>750 nm</td>
</tr>
<tr>
<td>Beam diameter</td>
<td>2cm</td>
</tr>
<tr>
<td>Temporal shot to shot reproducibility</td>
<td>+/- 5 fs</td>
</tr>
<tr>
<td>Maximum laser intensity</td>
<td>$7 \times 10^{15}$ W/cm$^2$</td>
</tr>
</tbody>
</table>
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3.3.1 Titanium-Sapphire Femtosecond Laser

The titanium-sapphire oscillator (Spectra-Physics model: 3960 C) is the source of the femtosecond pulses. The laser is a self-mode locking system, using neither a mode locking dye nor an electrical device to select a mode. The frequency of the mode locked operation is 82 MHz. The solid state lazing medium, sapphire doped with titanium ions, is pumped by all the lines emitted from the Argon ion laser (Spectra Physics model: BeamLok™ 171).

Table 3.3: Laser output characteristics of the Ti-sapphire laser.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Output energy</td>
<td>10 nJ/pulse</td>
</tr>
<tr>
<td>Wavelength</td>
<td>750 nm</td>
</tr>
<tr>
<td>Output Power</td>
<td>0.82 W</td>
</tr>
<tr>
<td>Rep Rate</td>
<td>82 MHz</td>
</tr>
<tr>
<td>Bandwidth</td>
<td>60 nm</td>
</tr>
</tbody>
</table>

The Ti-sapphire laser produces wavelengths of 730 to 800 nm of fundamental light. A single wavelength can be selected by spreading out the band of wavelengths using a prism pair so that a spectral plane is formed between them. An adjustable slit, inside the titanium-sapphire, spatially selects a wavelength from the spectral plane. The bandwidth is limited by the reflectivity wavelength range of the dielectric mirrors in the system. The beam characteristics of the Ti-sapphire laser are set out in Table 3.3.

3.3.2 Argon Ion Laser

The function of this continuous wave, gas phase laser is simply to pump the titanium-sapphire laser. The argon atoms are ionized by electron collision in a high current discharge. The ions are excited by further electron collisions up to a group of energy levels (4p) which are about 35 eV above the atomic ground state. The electronic excitations are a result of multiple collisions since the electron energies are only a few electron volts. A population inversion forms between the 4p and 4s
level so that a series of stimulated lines are emitted. The strongest emitted lines are given in the Table 3.4.

Table 3.4: Beam characteristics for the argon ion laser.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Output Power</td>
<td>6-10 W</td>
</tr>
<tr>
<td>Wavelengths</td>
<td>488 nm, 514 nm, 540 nm</td>
</tr>
</tbody>
</table>

3.3.3 Chirping and Translation Optics

The duration of the pulses from the oscillator cavity is very short (55 fs) and pulse energy is of the order of nanojoules. These pulses are amplified, by a factor of 1000, by a chain of three power amplifiers. The short pulse duration would, if not increased, result in the power of the amplified pulses being so great as to produce a reduced beam quality due to non-linear effects. The pulse lengthening procedure is part of what is known as chirped-pulse amplification. The pulses from the Ti-Sapphire are beam steered through two pairs of prisms, PP1 and PP2 shown in Figure 3.19, that stretch the temporal length of the pulses by a factor of 14.5 to 800 fs. This procedure negatively chirps the pulses which means that the distribution of the wavelengths within the pulse has been temporally dispersed. As a result the power of the pulses has been decreased below a level which would impair the quality of the beam and the pulses can then be amplified in the three-stage amplifier with little distortion of the beam quality. Once the amplification process is complete the pulses can be recompressed to their original, non-temporally dispersed, state by positively chirping, or compressing, them.

3.3.4 The Nd-YAG Nanosecond Laser

This nanosecond laser, manufactured by Quanta Ray and used as a pump for the dye cell amplifier, is injection seeded and Q-switched. The output from the Ti-sapphire is synchronized with the output from the Nd-YAG by a photodiode reference signal. The fundamental wavelength (cavity output), 1064 nm, is frequency doubled to
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the required wavelength (532 nm), using a KDP crystal. Since the nanosecond laser performs only one task, to pump the amplifier medium, it is unnecessary for it to contain sophisticated components such as a Pockels cell or mode locking device. Table 3.5 gives a summary of the beam characteristics of the nanosecond Nd-YAG laser.

Table 3.5: Nd-YAG laser beam characteristics.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Output energy</td>
<td>300 mJ</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Pulse length</td>
<td>8 ns</td>
</tr>
<tr>
<td>Wavelength</td>
<td>532 nm</td>
</tr>
</tbody>
</table>

3.3.5 Pulsed Dye Amplifier

The amplification of the beam is a three-stage process. Three cells are filled with constantly flowing dye (LDS-571) which is pumped by the 532 nm Nd-YAG light. The photons from the Ti-Sapphire (750 nm) are then passed through the dye and amplified.

Figure 3.20: Schematic of the pulsed dye amplifier.
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A 10 cm focal lens, L1, was placed before the first dye cell, as shown in Figure 3.20, to focus the amplified beam through a 100 µm pinhole, l3, placed immediately after the first dye cell. The pinhole was used in order to reduce contamination of the beam from amplified spontaneous emission that is not spatially collimated.

A Bethune cell is used to contain the dye for the last stage of amplification. The beam profile of the Nd-YAG pump laser is annular. The cylindrical lens, CL, focuses the light in the first two stages of amplification down to a linear profile, such that the nanosecond pulses uniformly pump the dye. In the last stage of amplification both the primary beam and the pumping beam profiles have a larger cross sectional area. Using a cylindrical lens to focus the larger annular pumping beam profile does not result in a uniform cross sectional area, as shown in Figure 3.21. The Bethune cell evenly distributes the pumping light over the path of the primary beam, as also shown in Figure 3.21.

![Diagram](Figure 3.21: Function of the Bethune cell in the third stage of amplification of the femtosecond pulses.)

3.3.6 Optical Transport System of the Femtosecond Beam into the Vacuum Chamber

The steering and manipulation of the beam into the chamber was achieved as shown in Figure 3.22.
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Figure 3.22: The manipulation of the femtosecond beam into the vacuum chamber.

Once the beam had been compressed to 55 femtoseconds by the compressor block it was steered by two mirrors to the chamber. The chamber was made parallel with the optical bench so that vertically polarized light was parallel with the axis of the TOF mass spectrometer. The beam was steered, by M7 and M8, as shown in Figure 3.22 onto the centre of the entrance window, EW1 and the position of the beam was confirmed to be central on the exit window, EW2. A half wave plate, HWP, and polarizer, P, positioned in the beam path, as shown in Figure 3.22, were used to control the intensity and polarization of the beam. M7 was mounted on a 45° adjustable optical mount such that it could be removed from the beam path when the beam energy measurements were taken, as shown in Figure 3.22.

3.3.7 Optical Alignment of the Beam into the Vacuum Chamber

The in-vacuum focusing mirror mount, designed in the shape of a Maltese cross, is 2 mm smaller than the size of the laser beam, as shown in Figure 3.23. The mirror mount had been carefully positioned in the chamber to be concentric with the axis of the beam through the chamber.
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Figure 3.23: The in-vacuum focusing mirror and mount. The silhouette of the mount at the vacuum chamber exit is shown on a screen (S) after the EW2 window.

The beam exiting the vacuum chamber was observed on a screen and the shape of the Maltese cross shadow within the beam image was made symmetric by adjusting M8, as shown in Figure 3.22. The half wave plate, HWP, and polarizer, P, were placed in the beam path. The angular settings of the HWP and P for transmission of laser light with particular polarization directions had been determined as described in Section 3.2.4. Once the alignment procedure had been accomplished two adjustable irises, I4 and I5, were placed in the beam path, so that if the beam or beam steering mirrors moved, the alignment could easily be reset.

3.4 Gating of the Pulses

The gating of the pulses limited the pulse to pulse intensity variations for the laser. The gating window was set to +/- 5% of the intensity. A glass plate, GP, was placed in the path of the beam reflecting a fraction of the laser light into a photodiode, PD, as shown in Figure 3.24. The resulting voltage pulse from the photodiode was observed as an oscilloscope trace. The signal from the photodiode was then fed, via the oscilloscope, into the single channel analyzer, SCA, as shown in Figure
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3.24. The SCA was used to discriminate both an upper level and lower level of the pulse, so that the window width was 10% of the pulse height. The TTL output of the SCA was then fed in parallel to another channel of the oscilloscope and into the MCS as a start pulse.

![Figure 3.24: The apparatus arrangement for the gating of the start pulses for the mcx.](image)

3.5 Summary

This chapter has included a description of the Nd-YAG picosecond laser used in the present work to investigate multi-electron dissociative ionization in the intermediate regime and also the femtosecond system used in the present work to investigate multi-electron dissociative ionization in the tunneling regime. A description of the characteristics of the components of the femtosecond system has been given. Also included was a description of the transport and focusing methods and polarization determination.
Chapter 4: Measurement of the Laser Intensity

4.0 Laser Intensity Determination

The question of how laser intensity is determined has been answered in several ways, but universal and accurate absolute measurements of laser intensity have yet to be devised. Most experimentalists have calculated the peak laser intensity of the laser assuming a variety of spatial and temporal distributions. For peak intensity determination direct measurements of laser pulse duration, beam energy (or pulse energy) and focal spot size are made. The methods by which the measurements are taken, however, vary.

L'Huillier et al, 1983a and 1983b, measured the pulse energy using a calorimeter and the pulse duration was determined using an electro-optic streak camera coupled to a storage video system (Lompre et al, 1975). They found that the variation of the pulse duration was ±10%. The temporal distribution of the laser pulse, determined from the streak camera, was found to be given by Equation 4.1.

\[ G(t) = \cosh^{-1} \left( 2.63 \frac{t}{\tau} \right) \]  

Equation 4.1
where \( t \) is the time variable and \( \sigma \) is the temporal FWHM of the pulse. The spatial distribution was found not to vary during the duration of the laser pulse and was determined by photometric measurements (Morelec et al, 1976). Photographs of the focal region were taken in a set of planes perpendicular to the laser axis and were analysed by isodensitometry, the contours of which are given in Figure 4.1. The diameter of the focal region was determined to an accuracy of \( \pm 33\% \).

\[
I(x, y, z, t) = I_M F(x, y, z) G(t) \quad \text{Equation 4.2}
\]
where \( I_M \) is the maximum intensity, \( I_M = \frac{\varepsilon_l}{\tau S_o} \), \( F(x,y,z) \) is the spatial distribution, \( G(t) \) is the temporal distribution, \( \varepsilon_l \) is the laser pulse energy, \( \tau \) is the laser pulse duration and \( S_o \) is the area of the focal plane.

Frasinski \textit{et al}, 1987, spatially selected the Airy disc of the beam, which was known to contain 70\% of the beam energy, and focused it to a tight spot. The temporal shape of the laser pulse was approximated by a \( \text{sech}^2 \) distribution. The laser wavelength was known, the pulse FWHM was determined by an autocorrelator and the pulse energy was measured (±20\% pulse to pulse variations) and, hence, from these variables the peak intensity of the pulse was determined. Perry \textit{et al}, 1988, stated that to accurately determine the laser intensity it was important to find the variation, not only of the shot to shot energy of the pulses, but also the peak power of each laser pulse such that the pulse duration could be determined. This shot to shot power measurement was necessary since their laser system produced pulse duration fluctuations of as much as 15\% shot to shot. A 4\% reflection from the entrance window of the vacuum chamber was beam split such that 20\% was diverted to a calibrated photodiode to provide an energy measurement and 80\% was collimated and passed through a KDP crystal. The crystal was tuned such that the second harmonic output signal was proportional to the square of the fundamental intensity. The 2nd harmonic was separated from the fundamental wavelength and was passed into another photodiode. This signal was proportional to the product of the laser power and energy. Together with the independent measurement of energy a determination of the maximum laser intensity per shot was made. Perry \textit{et al}, 1988, found that it was unnecessary to measure the other variable, the focal volume, on a shot to shot basis since, as for L’Huillier \textit{et al}, 1983a, they found that the spatial distribution of the pulse did not alter. The intensity was determined using a \( \text{sech}^2 \) temporal distribution determined by autocorrelation and by combining the parameters as in Equation 4.2.

Various theories were found to produce ionization rates for noble gases for increasing intensity which could be compared well with experimental results (Augst \textit{et al}, 1991). The usefulness of this for laser intensity determination has been appreciated by nearly all the research groups working in this field. However, the calibration of peak intensity, using various different methods, was often used to corroborate
the intensity determination from the noble gas experiments. Chin et al, 1988, compared the ionization rates of Xe and Kr on their intensity scale with those determined by the modified Keldysh theory (Szoke et al, 1987). A comparison between experiment and theory for two laser pulse durations, 90 fs and 22 fs, are given in Figure 4.2. The Xe$^+$ data fitted the theory well; however, the comparison was not good for all ionization stages. A comparison of intensity determination for the xenon experiments was made with a determination from calculations of peak intensity. They made focal spot measurements by scanning a 5 μm pinhole across the laser focus and observing the portion of the energy transmitted through a pinhole. The beam spatial profile was found to be Gaussian and an autocorrelator was used to determine the average FWHM of the temporal distribution of the pulses.

\[ I \propto \int |u(t)|^2 dt \]

\[ I \propto \int |u(t)|^4 dt \]

Figure 4.2: Ion yield of xenon for experiments using 90 fs and 22 fs (Chin et al, 1988). The solid curves are calculated from the modified Keldysh theory (Szöke et al, 1987).

Perry et al, 1988, compared lowest order perturbation theory (LOPT) with the xenon ionization experiment calibrated using the peak intensity determination, previously explained in this section, as shown in Figure 4.3. They found that even in the intermediate regime (1 < \( \gamma < 4 \)) the LOPT was an adequate fit to the data.
When Augst et al., 1989, determined the focal spot size by equivalent target plane measurements using 2m and 15 cm focal length lenses, they found that the focal spot did not vary in size on a shot to shot basis. The energy of each laser shot was measured by taking a 4% reflection from a beam splitter and a correlation technique was used to measure the pulse FWHM (Albrecht et al., 1981). From these measurements an intensity scale was determined and used to calibrate the appearance intensities for the different stages of ionization for noble gases. They compared these intensity values to appearance intensities predicted from a simple classical model where a static electric field is superimposed on the Coulomb potential of the atom. Ionization occurs when suppression of the barrier decreases to the ionization level of the atom or ion. In a continuation of their investigations Augst et al., 1991, presented ionization experiments on Xe, Kr, Ar, Ne and He and plotted graphs of count rate for the different stages of ionization against the intensity scale determined in Augst et al., 1989. They were able to show good agreement of the ionization curves with the Ammosov-Delone-Krainov (ADK) theory, as shown in Figure 4.4 (Ammosov et al., 1986). Since this was the case, Zavriyev et al., 1993, used the xenon data of Augst et al., 1989, to calibrate their laser intensity.
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Figure 4.4: Comparison of the xenon ion production and that predicted by ADK theory (Augst et al, 1991).

Corkum et al, 1989, departing slightly from the trend towards investigation of xenon ionization rates measured the energy of the ponderomotively accelerated electrons coming from the laser focus and used Equation 4.3 to determine the intensity in the laser focal volume.

\[
\Phi_{\text{pond}} (eV) = \frac{e^2 E^2}{4m \omega^2} = 9.33 \times 10^{-14} I \lambda^2
\]

Equation 4.3

where \( \Phi_{\text{pond}} \) is the ponderomotive potential, \( e \) is the electric field strength of the laser (V/m), \( \omega \) is the frequency of the laser light (Hz), \( I \) is the laser intensity (W/cm\(^2\)), \( \lambda \) is the laser wavelength (\( \mu \)m) and \( e \) and \( m \) are the charge and mass of the electron respectively. The uncertainty of the intensity determined in this way was a factor of two.

Researchers began comparing their own experiments of xenon ionization with previous work in which the laser intensity had been determined by comparing
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experiments with theory such that there was a direct comparison between different experimentalists’ intensity determinations. Experimental results of the ionization of xenon had shown that several parameters could be used for comparison. The appearance intensity, $I_{\text{app}}$, is the intensity at which the ions are detected. The number of ions at the appearance intensity, however, has varied. For example, Perry et al., 1988, suggested that it occurs when a ‘small number’ of ions are detected while Augst et al., 1989, stated more precisely that the appearance intensity has been reached when 10 ions are detected. The saturation intensity, $I_{\text{sat}}$, is the intensity at which the depletion of the species of ion/atom/molecule in the focal volume takes place and is also the point of departure from linearity of the ionization rate. The experimental results of the intensity dependence of ionization do appear to result in a linear graph of ion counts as a function of laser intensity on a log/log scale. However, theories such as ADK do not even predict linearity of the function. Finally, the ionization rate itself has been used as a comparison and the linear gradient of a graph of the number of ions as a function of laser intensity on a log/log scale used to predict the number of photons in the interaction. However, this model, based on perturbation theory, is only applicable to the multiphoton regime and, perhaps, part of the intermediate regime (Perry et al., 1988).

Strickland et al., 1992, measured the dependence of the ionization rates of $\text{Xe}^+$ and $\text{Xe}^{2+}$ on intensity by calibrating a laser intensity scale using previous xenon ionization data (Chin et al., 1988), specifically the appearance intensity of $\text{Xe}^+$. Similarly, Dietrich et al., 1993, measured the xenon ionization rates against an uncalibrated intensity scale and then fitted the results to the atomic tunnelling model (Ammosov et al., 1986). However the intensity scale calibrated in this way was a factor of two different from that of Strickland et al., 1992. Dietrich et al., 1993, also calculated the relative intensity of the laser pulses by measuring the pulse energy and focal spot size. The focal volume was estimated using a spatial filter to select the Airy disc of the beam and carrying out lens focusing calculations. There was good agreement between this intensity determination and from the determination which used measurements of xenon ionization rates. Zavriyev et al., 1993, used the xenon data of Augst et al., 1989, to calibrate their intensity scale. Kumar et al., 1994, used three techniques to calibrate their intensity scale. Firstly, they measured the spot size by measuring the diameter of the burn mark on high-resolution photographic paper using a microscope. The pulse width and wavelength
were known and the average pulse energy was measured. From these parameters an intensity scale was determined. The second technique involved carrying out an experiment to determine the appearance intensity, $I_{a p p}$, of $Xe^+$ and comparing it to the theoretical prediction by Chang et al, 1993, who derived appearance intensities and saturation intensities for xenon by solving rate equations. The third technique involved the measurement of the saturation intensity, $I_{s a t}$, of $Xe^+$ and comparing this to the calculated value of $4 \times 10^{13}$ W/cm$^2$ reported by Perry et al, 1988.

To date the comparison of noble gas ionization parameters seems to be the best method to determine laser intensity scales and has been used to calibrate both the picosecond and femtosecond laser intensities used in experiments presented in this thesis.

4.1 Picosecond Intensity Determination Procedures

Two methods were used in the present work to determine the peak intensity of the focused picosecond laser pulses: Firstly, an approximate method in which a calculated focal volume and assumed spatially circular and temporally square pulse combine to give a peak intensity value and secondly, a comparison with previous ionization experiments on xenon (Perry et al, 1988).

4.1.1 Gaussian Optic Calculation of Focal Plane Area

The peak intensity of the beam was determined by assuming both a temporally square and a spatially circular laser pulse distribution. A calorimeter placed before the laser entrance window, EW1, was used to determine the average power of the beam. The pulse duration was 35 ps and the pulses were produced with a repetition rate of 20 Hz. These parameters, together with the area of the focal plane, allowed an estimation of the peak intensity of the laser, as shown in Equation 4.4.

$$I_p(W/cm^2) = \frac{P_A(W)}{\nu(Hz) \tau(s) A(cm^2)} = 2.1 \times 10^{13} \frac{P_A(W)}{cm^2}$$

Equation 4.4
where $I_p$ is the peak laser intensity, $P_a$ is the average power of the laser beam, $v$ is the repetition rate of the laser, $\tau$ is the pulse duration and $A$ is the area of the focal plane.

The focal area of the beam was determined using Gaussian optic calculations beginning at the exit of the laser beam from the laser and along the optical path consisting of three mirrors, two linear polarizers, two half-wave plates and a focusing lens and ending at the focal volume. The initial beam diameter was 9 mm with a divergence of 1 mR. The principal equations used for this Gaussian beam propagation calculation are shown in Equations 4.5 and 4.6 (Yarvi, 1976).

\[
R(z) = z \left[ 1 + \left( \frac{\pi \omega_0^2}{\lambda z} \right)^2 \right] \quad \text{Equation 4.5}
\]

\[
\omega^2(z) = \omega_0^2 \left[ 1 + \left( \frac{\lambda z}{\pi \omega_0^2} \right)^2 \right] \quad \text{Equation 4.6}
\]

where $R(z)$ is the radius of curvature of the beam at $z$, $\omega_0$ is the minimum waist of the beam, $\lambda$ is the wavelength of the laser light and $\omega(z)$ is the waist of the beam at $z$. The laser spot diameter was calculated to be 66 $\mu$m. Therefore, assuming a temporally square and spatially circular pulse, the maximum intensity can be worked out using Equation 4.5 to be $8.9 \times 10^{12}$ W/cm$^2$ for a laser power of 0.42 W, when the laser was operating at 20 Hz.

### 4.1.2 Xenon Ionization Measurements

The determination of the saturation intensity is achieved by observing the break from linearity of a graph of the number of xenon ions detected as a function of laser intensity on a log/log scale (explained in Section 4.0). Figure 4.5 shows the point on just such a graph at which the saturation of Xe$^+$ ions occurs (L'Huillier et al, 1983a). Similar saturation intensity determinations can be made from the xenon ionization
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curves given in Perry et al, 1988, shown in Figure 4.7. The saturation intensities of the first three stages of ionization are given in Table 4.1.

\[ \begin{align*}
Xe^+ & : 10^{11} \text{ eV} \\
Xe^{2+} & : 45 \text{ eV} \\
Xe^{3+} & : 12 \text{ eV}
\end{align*} \]

Figure 4.5: A graph of the number of xenon ions as a function of laser intensity on a log/log scale. The dashed line indicates the saturation intensity, \( I_{\text{sat}} \) (L'Huillier et al, 1983a).

An experiment was carried out to determine the relationship between the number of ions per pulse produced by the interaction of the laser as a function of laser intensity, the wavelength of which was 532 nm with a 35 ps pulse duration. The experimental apparatus arrangement has been described in Section 2.1 and 3.2.4, but, briefly, the laser beam was guided by three mirrors into a sealed vacuum chamber via two linear polarizers and two half-wave plates. A 50 mm convex lens focused the beam into the interaction region. The xenon gas entered the chamber as a diffuse beam perpendicular to the TOF axis and the laser beam. The ions were extracted by an electric field and spatially focused by the TOF system onto the channel plate detector.

A calorimeter was placed at the laser exit window of the chamber and the average power reading was monitored throughout the experiment such that the error of the average power was \( \pm 10\% \). The relationship between the average power reading at the laser exit and entrance to the chamber had been determined prior to the experiment. Spectra were recorded for a range of average power readings. The counts detected for each ion species were plotted against the average power at the
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chamber entrance window on a log/log graph and the saturation intensity determined for each xenon ion species.

\[ \text{Table 4.1} \]

<table>
<thead>
<tr>
<th>No. of counts</th>
<th>Xe$^+$</th>
<th>Xe$^{2+}$</th>
<th>Xe$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity (W/cm$^2$)</td>
<td>$10^{13}$</td>
<td>$10^{14}$</td>
<td>$10^{15}$</td>
</tr>
</tbody>
</table>

Figure 4.6: TOF spectrum of the xenon ionization recorded with a 300 V/cm extraction field for an average power reading of 0.42 W.

The data was collated in Table 4.1 and compared to results given in Perry et al, 1988, who used a laser wavelength of 586 nm. Their maximum intensity was $6 \times 10^{14}$ W/cm$^2$ and their lowest intensity $2.5 \times 10^{13}$ W/cm$^2$. Thus, the range of the Keldysh parameter for the xenon experiments in Perry et al, 1988, is 2.75 to 0.56 which is within the intermediate regime for intense laser ionization.

Figure 4.7: Number of ions detected as a function of laser intensity for xenon (Perry et al, 1988).
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Table 4.1: The comparison between the 35 picosecond data (present data) and Perry et al, 1988.

<table>
<thead>
<tr>
<th>Xenon ion</th>
<th>Saturation intensity (W/cm²) (Perry et al, 1988)**</th>
<th>Average power at which saturation occurs (W) (Present work)***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe⁺</td>
<td>$5 \times 10^{13} \pm 1 \times 10^{13}$</td>
<td>$0.06 \pm 0.01$</td>
</tr>
<tr>
<td>Xe²⁺</td>
<td>$1.5 \times 10^{14} \pm 5 \times 10^{13}$</td>
<td>$0.17 \pm 0.02$</td>
</tr>
<tr>
<td>Xe³⁺</td>
<td>$2 \times 10^{14} \pm 5 \times 10^{13}$</td>
<td>$0.25 \pm 0.03$</td>
</tr>
</tbody>
</table>

** error estimated for extracting data from the graph of Perry et al, 1988, shown in Figure 4.5.

*** error taken as ±10% average power within which each experiment was conducted.

The values in Table 4.1 were used to determine the approximate intensity of the pulses in the beam from the average beam power values. The measured average power in the beam is linearly proportional to the energy in the laser pulses. The energy ion the laser pulses is directly proportional to the laser intensity. A linear calibration graph has been determined and was used to determine the intensities of spectra recorded at different average laser beam power values. The determination of the calibration graph, shown in Figure 4.7b, is tentative due to the scarcity of data.

![Figure 4.7b](image)

Figure 4.7b: The calibration graph determined from measured average power readings and Perry et al, 1988 for the saturation intensities of the first three stages of xenon ionisation.

Comparison between the intensity scale determined in this way and the determination from the peak intensity calculation given in Section 4.2.1 shows that the calibrated scales differ by a factor of 39 with the peak intensity calculation being the smaller. Gibson et al, 1990, pointed out that simply dividing the power in the beam by the area of the focal plane for a Gaussian spatial distribution means that the laser intensity is actually 3.67 times greater than anticipated. However, the
xenon ionization method gives an intensity range that compares well with other groups who use lasers of similar specifications (for example Mathur et al., 1994) and is, therefore, the method used for the calibration of the intensity for the present picosecond work. The range of focused intensities used in picosecond laser experiments presented in Chapter 5 was determined to be $2.1 \times 10^{13}$ W/cm$^2$ to $3.5 \times 10^{14}$ W/cm$^2$. The Keldysh parameter range for these intensities for xenon is 3.31 to 0.87 which places the experiment in the intermediate range for the Keldysh parameter.

4.2 Femtosecond Intensity Determination Procedures

Two methods were used to determine the peak intensity of the focused femtosecond laser pulses: Firstly, an intensity determination involving the calculated focal volume and measured pulse duration and energy and secondly, a comparison with previous xenon data (Augst et al., 1989).

4.2.1 Peak Power Calculations

A pyrometer was placed in the beam and the beam energy, $E$, was measured. The temporal FWHM of the pulse was determined by autocorrelation.

The laser intensity, calculated for a Gaussian spatial distribution, corresponds to 86% of the pulse energy averaged over a radius at which the intensity is down to $1/e^2$ of the peak intensity value and can be calculated from Equation 4.10.

$$I = \frac{0.86xExEff}{100xD^2\pi(1.5xG_w)^2}$$  \hspace{1cm} \text{Equation 4.10}

where $I$ is the laser intensity (W/cm$^2$), $E$ is the pulse energy at the laser exit (J), $Eff$ is the fraction of energy that is transmitted into the vacuum chamber due to loss of energy at the transport optics (0.75) and $D$, is the pulse duration (s). The Gaussian waist, $G_w$, of the spatial distribution of the focused spot is calculated from $\frac{2f\lambda}{\pi D}$.
where \( f \) is the focal length of the focusing mirror (2.1 mm), \( \lambda \) is the laser wavelength and \( D \) is the diameter of the laser beam. The diameter of the focused beam calculated in this way is 4.2 \( \mu \)m. The maximum laser intensity calculated from Equation 4.10 for the femtosecond laser is \( 7.2 \times 10^{15} \text{ W/cm}^2 \).

The laser intensity can also be calculated assuming a flat-topped spatial distribution. The laser intensity is calculated from the averaged energy of the Airy disc which contains 84% of the pulse energy and can be determined using Equation 4.11.

\[
I = \frac{0.84EXEff}{100xDT\pi(1.2w)^2}
\]

Equation 4.11

which uses the same notation as for Equation 4.10 except that \( w \) is the waist calculated from \( \frac{1.22f\lambda}{D} \) where \( f \) is the focal length of the focusing mirror, \( \lambda \) is the laser wavelength and \( D \) is the diameter of the laser beam. The maximum laser intensity for the femtosecond laser calculated by this method is \( 3 \times 10^{15} \text{ W/cm}^2 \).

### 4.2.2 Xenon Ionization Measurements

The second method that was used to determine the intensity was to determine the appearance intensities for the stages of ionization of xenon. The apparatus has been described in Sections 2.1 and 3.3.6 but, briefly, the femtosecond beam was guided by two mirrors through a half wave plate and a polarizer into the vacuum chamber. The beam was then reverse focused, as shown in Figure 3.24, by a f/2 parabolic mirror. The xenon gas entered the chamber as a diffuse beam perpendicular to the laser beam and the TOF axis. The ions were extracted by an electric field and spatially focused by the TOF system onto the channel plate detector. The energy of the beam was gated by diverting the 4% reflected beam from the chamber entrance into a photodiode as described in Section 3.5. The photodiode outputs were compared to the energy readings of a single shot energy meter and the relationship was found to be linear. TOF spectra were recorded for
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different pulse energies and the ion counts per pulse determined for each stage of ionization plotted on a graph, as shown in Figure 4.8.

![Graph of ion counts per laser pulse vs photodiode output (mJ)](image)

**Figure 4.8:** The relationship between the xenon ions per laser pulse and the photodiode signal which was proportional to the femtosecond laser beam energy. Ionization stages 6 and 7 have been removed from the graph for clarity.

The energy values for the appearance intensities of the xenon ions were compared to the appearance intensities, $I_{app}$, determined by Augst et al., 1989, shown in Figure 4.9. Augst et al., 1989, defined the appearance intensity as the value at which 10 ions per pulse are detected. Comparing their focal volume and gas pressure to those in the present work it was calculated that the equivalent number of ions in the present work was 0.008 ions per laser pulse which was defined as the $I_{app}$, as shown in Figure 4.8.

![Graph of ion appearance intensity vs ionization potential (eV)](image)

**Figure 4.9:** Ion appearance intensity vs ionization potential for xenon (Augst et al., 1989).
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A comparison of the appearance intensities of xenon for the present work and that of Augst et al., 1989, is given in Table 4.2. The maximum intensity of Augst et al., 1989, was $5 \times 10^{16}$ W/cm$^2$ and the lowest intensity was $1.5 \times 10^{14}$ W/cm$^2$. Thus the range of the Keldysh parameter for Augst et al., 1989, is 0.03 to 0.63, which places the experiments in the tunnelling regime for intense laser ionization of xenon.

Table 4.2: The comparison between the present 60 femtosecond data and Augst et al., 1989.

<table>
<thead>
<tr>
<th>Xenon ion</th>
<th>Appearance intensity (W/cm$^2$) (Augst et al, 1989)**</th>
<th>Photodiode signal at which ions appear (mV) (Present work)***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe$^+$</td>
<td>$7 \times 10^{13} \pm 1 \times 10^{13}$</td>
<td>13 $\pm$ 0.1</td>
</tr>
<tr>
<td>Xe$^{2+}$</td>
<td>$1.5 \times 10^{14} \pm 5 \times 10^{13}$</td>
<td>40 $\pm$ 2</td>
</tr>
<tr>
<td>Xe$^{3+}$</td>
<td>$4 \times 10^{14} \pm 5 \times 10^{13}$</td>
<td>80 $\pm$ 4</td>
</tr>
<tr>
<td>Xe$^{4+}$</td>
<td>$8 \times 10^{14} \pm 1 \times 10^{14}$</td>
<td>115 $\pm$ 5.8</td>
</tr>
<tr>
<td>Xe$^{5+}$</td>
<td>$1.5 \times 10^{15} \pm 5 \times 10^{14}$</td>
<td>204 $\pm$ 10.2</td>
</tr>
</tbody>
</table>

** error estimated for extracting data from the graph of Augst et al, 1989, shown in Figure 4.7.

*** error is the $\pm5\%$ average power within which each experiment was conducted.

A conversion between the average laser power and the intensity can then be determined by Equation 4.12:

$$\text{Intensity} = \frac{I_{\text{app}}(\text{Xe}^+)}{E(\text{Xe}^+)} = \frac{7 \times 10^{13} E}{13} = (5.4 \times 10^{12} \pm 8.8 \times 10^{11}) E \quad \text{Equation 4.12}$$

where $I_{\text{app}}(\text{Xe}^+)$ is the appearance intensity of Xe$^+$ (from Augst et al., 1989), $E(\text{Xe}^+)$ is the energy of the laser beam at the appearance intensity of Xe$^+$. The normalisations of the $I_{\text{app}}$ of the second, third, fourth and fifth stages of ionization of xenon are collated in Table 4.3.

The appearance intensities of the differently charged xenon ions provide a calibration scale for the intensity of the femtosecond laser data. The calibration graph was determined in the same way for the femtosecond data as for the picosecond data.
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Table 4.3: Summary of the normalisation equations determined from xenon ionization data (as shown in Equation 4.12 for Xe⁺).

<table>
<thead>
<tr>
<th>Xenon ion</th>
<th>Normalisation Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe⁺</td>
<td>((5.4 \times 10^{12} \pm 8.8 \times 10^{11})E)</td>
</tr>
<tr>
<td>Xe²⁺</td>
<td>((5.0 \times 10^{12} \pm 1.7 \times 10^{12})E)</td>
</tr>
<tr>
<td>Xe³⁺</td>
<td>((5.0 \times 10^{12} \pm 8.0 \times 10^{11})E)</td>
</tr>
<tr>
<td>Xe⁴⁺</td>
<td>((6.7 \times 10^{12} \pm 1.1 \times 10^{12})E)</td>
</tr>
<tr>
<td>Xe⁵⁺</td>
<td>((7.4 \times 10^{12} \pm 2.6 \times 10^{12})E)</td>
</tr>
</tbody>
</table>

The range of focused intensities used in experiments presented in this thesis was determined to be \(1.2 \times 10^{14}\) to \(7 \times 10^{15}\) W/cm². This value is confirmed by the fact that the appearance intensity for Xe⁷⁺, the highest stage of ionization produced by the femtosecond laser, is \(6 \times 10^{15}\) W/cm² (Augst et al, 1989). The Keldysh parameter range for these intensities for Xe⁺ is 0.98 to 0.13 which places these experiments in the tunnelling range for the Keldysh parameter.

4.3 Summary

The intensity calibration for both the femtosecond and picosecond laser has been determined. The method that appeared to be most successful for both laser systems was to compare the graphs of xenon ionization to determine the laser beam energies to the saturation intensity, \(I_{\text{sat}}\), from Perry et al, 1988, for the picosecond system and to the appearance intensity, \(I_{\text{app}}\), from Augst et al, 1989, for the femtosecond system.
Chapter 5: Dissociative Ionization of Nitrous Oxide in Intense Picosecond and Femtosecond Laser Fields

5.0 Introduction

This chapter includes ion TOF spectra produced by laser dissociation of $\text{N}_2\text{O}$ using 532 nm wavelength light of 35 ps pulse duration, and 750 nm wavelength light of 60 fs pulse duration. The initial kinetic energies of the detected fragment ions have been calculated for both the picosecond and femtosecond laser data and will be discussed.

Nitrous oxide is a linear molecule in the ground electronic state, which does not have a centre of symmetry (Wells et al, 1984). The molecule has a permanent dipole moment, $\mu_p$, of 0.166 Debye (Shulman et al, 1950). The bond orders are 2.5 (N \equiv N) and 1.5 (N \equiv O) corresponding to the bond lengths $r_1 = 1.1257 \pm 0.0020$ Å and $r_2 = 1.186 \pm 0.0020$ Å respectively (Douglas and Moller, 1954), as shown in Figure 5.1.
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![Diagram of molecular arrangement with distances]

Figure 5.1: The molecular arrangement of the atoms of the nitrous oxide molecule.

5.1 Dissociative Ionization of N\textsubscript{2}O by 35 Picosecond Laser Pulses

Presented are the results of dissociative ionization of nitrous oxide when subjected to intense 532 nm laser light pulses with a 35 ps duration. The kinetic energies of the fragments are reported and several dissociation channels determined. The operating parameters appertaining to the picosecond experiments on N\textsubscript{2}O are listed in Table 5.1.

Table 5.1: The operating conditions for the data collected during the experiments on N\textsubscript{2}O with 35 picosecond laser pulses.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser repetition rate</td>
<td>20 Hz</td>
</tr>
<tr>
<td>Laser wavelength</td>
<td>532 nm</td>
</tr>
<tr>
<td>Laser pulse duration</td>
<td>35 ps</td>
</tr>
<tr>
<td>Laser intensity range</td>
<td>(2.12 \times 10^{13} - 1.34 \times 10^{18}) W/cm(^2)</td>
</tr>
<tr>
<td>Keldysh parameter</td>
<td>3.39 - 1.35</td>
</tr>
<tr>
<td>Extraction field range</td>
<td>25 - 300 V/cm</td>
</tr>
</tbody>
</table>

5.1.1 Results of the Dissociative Ionization of N\textsubscript{2}O by a 35 Picosecond Laser Field

Figure 5.2 shows a spectrum recorded when the polarization was perpendicular and parallel to the TOF axis. The ion peaks in the TOF spectra recorded when the laser field was perpendicular to the TOF axis were used to determine the zero positions, as discussed in Section 2.8.1. The 'zero position' of an ion species is the time of
flight of the ion which initially had zero momentum along the TOF axis.

Figure 5.2: TOF spectra of N₂O fragments resulting from dissociative ionization by 35 ps laser pulses at 532 nm, with a gas pressure of 1.0 x 10⁻⁷ mbar, an extraction field of 40 V/cm and a laser intensity of 1.4 x 10¹⁸ W/cm². The laser polarization direction was perpendicular to the TOF axis in the spectrum shown in black and parallel in the spectrum shown in red.

Each zero position was used as a reference to look for peaks which appear at exactly the same time interval either side. These symmetrically positioned peaks resulted from energetic ions dissociating, towards and away from the detector along the TOF axis.

In order to confirm that the TOF peaks were real, and not a function of instrumentation, the positions of the peaks on the TOF axis of the spectra in relation to their zero positions for different extraction fields were noted and the initial kinetic energies of the ions determined, as discussed in Section 2.8.1. Correct peak designation was confirmed when the kinetic energy values were the same, to within the error bars, for each extraction field.

The initial kinetic energies of the fragment ions produced by the picosecond laser, were determined from spectra recorded with three different extraction fields; 25, 40 and 75 V/cm. In Figures 5.3 to 5.10 the solid labeling lines show the ion positions that are easily discernable from the spectra. The dashed labeling lines show the ion peak positions that are less certain or have been deduced.
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Figure 5.3: The regions of the TOF spectra that include NO$^+$ and N$_2^+$ ions recorded with extraction fields of 25 V/cm, 40 V/cm and 75 V/cm. The laser polarization direction is parallel to the TOF axis. The laser intensity is $1.3 \times 10^{14}$ W/cm$^2$ and the ambient pressure $1.0 \times 10^{-7}$ mbar.

In the spectra shown in Figure 5.3 there is a distinct energy group of NO$^+$ ions, $a$, and two less distinct N$_2^+$ energy groups, $b$ and $c$, where $b$ is a zero energy group and $a$ and $c$ are of finite energy. Using the analytical technique described in Section 2.8.1 the peak energies of the NO$^+$ and N$_2^+$ ion groups were calculated for the three different extraction fields and are shown in Table 5.2.
Table 5.2: The NO$^+$ and N$_2^+$ energy groups deduced from spectra recorded with three different extraction fields.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Extraction field (V/cm)</th>
<th>Energy group, a (eV)</th>
<th>Energy group, b (eV)</th>
<th>Energy group, c (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$^+$</td>
<td>25</td>
<td>0.18 ± 0.03</td>
<td>0</td>
<td>not resolved</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.15 ± 0.03</td>
<td>0</td>
<td>0.28 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>0.20 ± 0.01</td>
<td>0</td>
<td>0.32 ± 0.06</td>
</tr>
<tr>
<td>N$_2^+$</td>
<td>25</td>
<td>0</td>
<td>not resolved</td>
<td>0.32 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0</td>
<td>0.28 ± 0.04</td>
<td>0.32 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>not resolved</td>
<td>0</td>
<td>0.32 ± 0.06</td>
</tr>
</tbody>
</table>

Figure 5.4 show the regions of the spectra that include the N$^+$ and O$^+$ ion peaks. There is only one O$^+$ energy group resolved, d, and two N$^+$ energy groups, e and f, where e is a zero energy group and f is a finite energy group. These ion peaks are curious as the N$^+$ signal is large at 0 eV and broad on the forward part of the peak, but appears to have a distinct backward peak, which is not O$^+$ thermal. The ion energies for varying extraction fields are shown in Table 5.3.

Figure 5.5 shows the ion peaks produced by the doubly charged ions, which are to a great extent merged together. The peak designations for the doubly charged fragment ions are less certain than for the other ions discussed in this section. Like N$^+$, N$^{2+}$ is very broad with little O$^{2+}$ signal. The ion peaks for two N$^{2+}$ energy groups (i and h) in the spectrum recorded with a 25 V/cm extraction field have been followed through to spectra recorded with extraction fields of 40 and 75 V/cm and one O$^{2+}$ energy group (g) has been followed through to the spectra with higher extraction fields.

The energies of the N$^{2+}$ ions found for each extraction field are shown in Table 5.3. Insufficient numbers of triply charged ions were detected to determine their energies.
Figure 5.4: The regions of the TOF spectra that include $N^+$ and $O^+$ ions recorded with extraction fields of 25 V/cm, 40 V/cm and 75 V/cm. The laser polarization is parallel to the TOF axis. The laser intensity is $1.3 \times 10^{14}$ W/cm$^2$ and the ambient pressure of $1.0 \times 10^7$ mbar.

Figure 5.5: The regions of the TOF spectra that include $O^{2+}$ and $N^{2+}$ ions recorded with extraction fields of 25 V/cm, 40 V/cm and 75 V/cm. The laser polarization direction was parallel to the TOF axis. The laser intensity was $1.3 \times 10^{14}$ W/cm$^2$ and the ambient pressure $1.0 \times 10^7$ mbar.
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Table 5.3: The energy groups for the singly and doubly charged nitrogen and oxygen ions from spectra recorded with three different extraction fields.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Extraction field (V/cm)</th>
<th>Energy group, d (eV)</th>
<th>Energy group, e (eV)</th>
<th>Energy group, f (eV)</th>
<th>Energy group, g (eV)</th>
<th>Energy group, h (eV)</th>
<th>Energy group, i (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O⁺</td>
<td>25</td>
<td>0.75 ± 0.13</td>
<td>0</td>
<td>0.86 ± 0.14</td>
<td>not resolved</td>
<td>4.00 ± 0.69</td>
<td>3.87 ± 0.80</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.16 ± 0.14</td>
<td>0</td>
<td>1.07 ± 0.13</td>
<td>6.02 ± 0.77</td>
<td>3.57 ± 0.53</td>
<td></td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>2.05 ± 0.22</td>
<td>0</td>
<td>1.32 ± 0.17</td>
<td>6.64 ± 1.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N⁺</td>
<td>25</td>
<td>not resolved</td>
<td>0</td>
<td>0.86 ± 0.14</td>
<td>4.00 ± 0.69</td>
<td>3.87 ± 0.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td></td>
<td>0</td>
<td>1.07 ± 0.13</td>
<td>3.57 ± 0.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>75</td>
<td></td>
<td>0</td>
<td>1.32 ± 0.17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O⁺⁺</td>
<td>25</td>
<td>not resolved</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N⁺⁺</td>
<td>25</td>
<td>not resolved</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.1.2 Analysis of Picosecond Laser Results

The forward and backward moving ion peaks of the same ion group should, for a symmetric extraction field, be symmetric in appearance. This is clearly not the case for the picosecond laser results, as shown in, for example, Figure 5.6a. There appear to be more ions detected in the forward moving ion peak. The angular resolution of the detector for forward and backward moving ions of these low energy ions are mostly 180° or slightly less for the backward moving ion, but not enough to account for the deficiency of ions in the backward peak. There is a saturation of signal from the forward moving ion peak to the backward that has been attributed to the multi-channel scalar (MCS).

Figure 5.6 shows the ion peaks for the NO⁺ and N₂⁺ ions for (a) the picosecond and (b) the femtosecond laser spectra. The input rate of data in the forward NO⁺ peak for the picosecond spectra is 6 MHz and the figure shows significant saturation of the backward moving NO⁺ ion peak, while the input rate of data in the forward
moving NO\(^+\) ion peak for the femtosecond spectra is 3.6 MHz and shows much less saturation of the backward moving NO\(^+\) ion peak.

\[\text{Figure 5.6: The ion peaks for the NO}^+\text{ and N}_2^+\text{ ions for (a) the picosecond and (b) the femtosecond laser spectra.}\]

Despite this saturation it is still possible to designate the peak positions of the energy distributions of the ions. Usually the forward moving ion peak is readily observable and since the zero position is known the few cases where the designation of the backward moving ion peak is debatable is less important since only the zero position and either the forward or backward moving ion peak position is necessary in order to determine the kinetic energy of the ion group. This section contains the tentative determination of some of the channels produced by dissociative ionization of N\(_2\)O in an intense picosecond laser field from the preliminary data given in Section 5.1.1.

The momenta parallel to the TOF axis, p\(_\parallel\), of ions from the a to j energy groups, have been calculated from the kinetic energies, given in Section 5.1.1, in order to determine which channels are opened in the dissociative ionization of N\(_2\)O by picosecond laser pulses. The technique of comparing the momenta, p\(_\parallel\), depends on an ion from a single channel being resolved from the same ion species with a different energy from a different channel. However, in the picosecond spectra under discussion ion energy distributions are produced rather than discrete energy values. Equating momenta values found from the peak energy of the distribution does not result in the determination of all the channels. Nevertheless, five channels have been tentatively determined by this technique and are shown in Table 5.4. The last column of the table shows the total dissociation energies for the channels. This is
determined by summing the energies measured for those ions found to have been produced in that channel. In some cases the ion momenta does not sum to zero for the peaks of the momenta distributions. However, the ion momenta for a particular channel could be incorporated within the momenta distribution produced by the ion peak. In this case the peak momenta for one ion are assumed to be summed to zero for the other ion groups in the channel and their energy deduced from that. This energy can then be added to the measured energy of the other ion groups in the channel.

Table 5.4: Channels of dissociative ionization of N₂O in a 35 picosecond laser field at a laser intensity of 1.3 x 10^{14} W/cm² and an ambient pressure of 1.0 x 10⁻⁶ mbar.

| Ion fragment | Kinetic energy (eV) | Momentum, \(|p| \times 10^{-22} (J/\text{kg}^{1/2})| \) | Channel | Experimentally determined total energy (eV) |
|--------------|---------------------|-----------------------------------------------|---------|---------------------------------------------|
| N₂⁺         | 0                   | 0                                             | N₂⁺ + O | 0                                           |
| NO⁺         | 0.18 ± 0.03         | 0.54 ± 0.22                                   | NO⁺ + N⁺ | 0.56 ± 0.14                                 |
| N⁺          | (0.86 ± 0.14)**     | (0.80 ± 0.32)**                               | N⁺ + O⁺ | 0.76 ± 0.14                                 |
| N₂⁺         | 0.28 ± 0.04         | 0.65 ± 0.24                                   | N₂⁺ + O⁺ | 0.76 ± 0.14                                 |
| O⁺          | (0.75 ± 0.13)**     | (0.80 ± 0.33)**                               | N⁺ + N + O⁺ | 1.61 ± 0.19                                 |
| O⁺          | 0.75 ± 0.13         | 0.80± 0.32                                    | N⁺ + N + O⁺ | 1.61 ± 0.19                                 |
| N⁵⁺         | 4.00 ± 0.69         | 1.72 ± 0.72                                   | N⁵⁺ + N⁺ + O⁺** | 10.41 ± 1.03                                 |
| N⁺          | (0)**               | (0)**                                         | N⁺ + N⁺ + O⁺** | 10.41 ± 1.03                                 |
| O⁺⁺         | 6.02 ± 0.77         | 2.26 ± 0.81                                   | N⁺ + N⁺ + O⁺** | 10.41 ± 1.03                                 |

** This value is the peak energy value of the distribution. This peak momenta value does not sum to zero with the other ion/s for this channel but within the momenta distribution there is an ion momenta that does.

5.1.3 Discussion of Picosecond Laser Results

The calculated energies given in Table 5.5 were determined from the Coulomb force equation. The molecule was assumed to be linear and to begin the Coulomb explosion when the constituent atoms were at the equilibrium distance. Equation 5.1 shows the formula used to determine the Coulomb energy for the tri-atomic nitrous oxide molecule.
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\[ E_t = E_{N_t \rightarrow N_t} + E_{N_t \rightarrow O_t} + E_{N_t \rightarrow O_t} \]  
\text{Equation 5.1}

where \( E_t \) is the total energy of the Coulomb dissociation, \( E_{N_t \rightarrow N_t} \) is the energy of the Coulomb dissociation of the terminal and central nitrogen ions, \( E_{N_t \rightarrow O_t} \) is the energy of the Coulomb dissociation of the central nitrogen ion and the terminal oxygen ion and \( E_{N_t \rightarrow O_t} \) is the energy of the Coulomb dissociation of the terminal nitrogen and terminal oxygen ions. The total energy of the Coulomb dissociation of \( \text{N}_2\text{O} \) into atomic ions is found from Equation 5.2.

\[ E_t = \frac{q(N_c)q(N_t)}{4\pi\varepsilon_0(r_1)} + \frac{q(N_c)q(O_t)}{4\pi\varepsilon_0(r_2)} + \frac{q(N_t)q(O_t)}{4\pi\varepsilon_0(r_1 + r_2)} \]  
\text{Equation 5.2}

where \( q(N_t) \), \( q(N_c) \) and \( q(O_t) \) are the charges on the terminal and central nitrogen ion and terminal oxygen ion respectively, \( \varepsilon_0 \) is the electric constant \( (8.85 \times 10^{-12} \text{ Fm}^{-1}) \) and \( r_1 \) and \( r_2 \) are the bond lengths between the terminal nitrogen and central nitrogen and between the central nitrogen and terminal oxygen respectively, as shown in Figure 5.1.

The Coulomb explosion energies of the molecular fragment ions were calculated by assuming that the charge of the molecular fragment ion originated from the central position of the diatomic molecular ion. The fragmentation of \( \text{N}_2\text{O} \) into \( \text{N}^{m+} + \text{NO}^{n+} \) is calculated using Equation 5.3 and the Coulomb explosion energies are given in Table 5.5. The same notation is used for Equation 5.3 as for Equation 5.2 and \( q(\text{NO}) \) is the charge on the NO ion.

\[ E_t = \frac{q(N_t)q(\text{NO})}{4\pi\varepsilon_0(r_1 + \frac{r_2}{2})} \]  
\text{Equation 5.3}

The Coulomb energy of the dissociation of \( \text{N}_2\text{O} \) into \( \text{N}_2^{m+} + \text{O}^{n+} \) is calculated in the same way as for the \( \text{N}^{m+} + \text{NO}^{n+} \) fragmentation, using Equation 5.4, and the Coulomb explosion energies are given in Table 5.5.
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\[ E_e = \frac{q(N_2)q(O_1)}{4\pi\varepsilon_0\left(\frac{r_1}{2} + r_2\right)} \quad \text{Equation 5.4} \]

Table 5.5: The Coulomb explosion energies of the dissociative ionization of \( \text{N}_2\text{O} \) fragmenting into ions calculated using Equation 5.2, 5.3 and 5.4 and assuming the Coulomb explosion begins at the atom equilibrium positions.

<table>
<thead>
<tr>
<th>( q(N_2) )</th>
<th>( q(N_3) )</th>
<th>( q(O_1) )</th>
<th>Total calculated energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>6.22</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>31.13</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>74.71</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>49.48</td>
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<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>50.13</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2</td>
<td>124.52</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( q(N_2) )</th>
<th>( q(\text{NO}) )</th>
<th>Total Calculated energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>8.37</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>16.74</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>16.74</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>33.48</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( q(N_2) )</th>
<th>( q(O_1) )</th>
<th>Total Calculated energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>8.23</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>16.45</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>16.45</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>32.90</td>
</tr>
</tbody>
</table>

The experimentally determined total kinetic energy release of the dissociative ionization channels are much less than the calculated Coulomb explosion kinetic energies. Table 5.6 shows the ratios of the calculated to the experimentally determined energies for the four tentatively determined Coulomb explosion channels. The ratios are not the same for each of the four channels as would be expected if the Coulomb explosions were simply occurring at a larger separation than the equilibrium separation, as observed experimentally (Posthumus et al, 1996) and predicted theoretically (Seideman et al, 1996 and Chelkowski and Bandrauk, 1995b).
Table 5.6: The ratio of calculated energy to experimentally determined energy for the four Coulomb explosion channels.

<table>
<thead>
<tr>
<th>Channel</th>
<th>Calculated energy, $E_C$ (eV)</th>
<th>Experimentally determined energy, $E_M$ (eV)</th>
<th>Energy Ratio $\left(\frac{E_M}{E_C} \times 100\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$^+$ + N$^+$</td>
<td>8.37</td>
<td>0.56 ± 0.14</td>
<td>6.69 ± 1.67</td>
</tr>
<tr>
<td>$N_2^+$ + O$^+$</td>
<td>8.23</td>
<td>0.76 ± 0.14</td>
<td>9.23 ± 1.70</td>
</tr>
<tr>
<td>N$^+ + N + O^+$</td>
<td>6.22</td>
<td>1.61 ± 0.19</td>
<td>25.88 ± 3.05</td>
</tr>
<tr>
<td>$N^2+ + N^+ + O^{2+}$</td>
<td>74.71</td>
<td>10.41 ± 1.03</td>
<td>13.93 ± 1.38</td>
</tr>
</tbody>
</table>

A likely explanation for the low experimental to calculated energy ratios, shown in Table 5.6, for three of the channels is Post Dissociative Ionization (PDI). The first two channels in the Table could be low energy dissociative ionization processes, followed by PDI to produce fragment ions that appear to be from Coulomb explosion processes. The fragment ions produced in this way would have the very low kinetic energies associated with dissociative ionization. This double process could also explain the appearance of the apparent $N^2+ + N^+ + O^{2+}$ channel in that it arises from the $N^+ + N^+ + O^+$ Coulomb explosion channel and is further ionized.

\[
\text{NO}^+ + N + h\nu \rightarrow \text{NO}^+ + N^+ \quad \text{or} \quad \text{NO} + N^+ + h\nu \rightarrow \text{NO}^+ + N^+ \quad \text{or} \quad \text{N}_2^+ + O + h\nu \rightarrow \text{N}_2^+ + O^+ \\
\text{and} \quad N^+ + N^+ + O^+ + h\nu \rightarrow N^2+ + N^+ + O^{2+}
\]

Since the PDI process does not add any kinetic energy to the fragment ions the energy assigned to the $N^2+ + N^+ + O^{2+}$ channel (10.41 eV) is actually associated with the $N^+ + N^+ + O^+$ channel. The experimental to calculated energy ratio for the $N^+ + N^+ + O^+$ channel is then 33.4%. The mean internuclear separation of the ions from which the Coulomb explosion occurs is calculated to be 3.5 Å. These processes can only occur, however, if no stabilization has occurred since, as explained in Section 1.7, if ionization is delayed to the end of the pulse there is no time for PDI before the pulse terminates.

The $N^+ + N + O^+$ channel has an experimental to calculated energy ratio of 25.9%, as shown in Table 5.6. This energy discrepancy is probably due to Coulomb explosion from a larger internuclear separation than the equilibrium separation.
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(Posthumus et al, 1995). The mean internuclear separation of the ions from which the Coulomb explosion occurs is calculated to be 4.5 Å.

Frasinski et al, 1991, found, using 0.6 ps duration laser light of 600 nm wavelength, that he could distinguish 2 channels; NO\(^+\) + N\(^+\) the total energy of which was between 4.7 and 6.3 eV, and N\(^{2+}\) + N\(^{2+}\) + O\(^{2+}\) the total energy of which was between 25.1 – 50.2 eV. The experimental to calculated energy ratio for the middle of this energy range is 30.2 %, which is a close to the energy ratio for the (1,0,1) channel (25.9 %) and for the (1,1,1) channel (33.4 %) deduced in this section. The NO\(^+\) + N\(^+\) channel energy found in this section and by Frasinski et al, 1991, differ significantly (0.56 eV and approximately, 5.5 eV respectively) suggesting that Frasinski et al, 1991, did detect the Coulomb explosion NO\(^+\) + N\(^+\) channel but that the apparent NO\(^+\) + N\(^+\) channel given in this section was in fact a low energy process followed by PDI.

5.1.4 Conclusion of the Picosecond Laser Results

The conclusion of this section is that the following processes have been tentatively determined:

\[ \text{N}_2\text{O} \rightarrow \text{NO} + \text{N}^+ \] or \[ \text{N}_2\text{O} \rightarrow \text{NO}^+ + \text{N} \] followed by a single ionization of the neutral

\[ \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^+ \] or \[ \text{N}_2\text{O} \rightarrow \text{N}_2^+ + \text{O} \] followed by a single ionization of the neutral

\[ \text{N}_2\text{O} \rightarrow \text{N}^+ + \text{N} + \text{O}^+ \] exploding from a mean internuclear separation of 4.5 Å

\[ \text{N}_2\text{O} \rightarrow \text{N}^+ + \text{N}^+ + \text{O}^+ \] exploding from a mean internuclear separation of 3.5 Å followed by single ionizations of the terminal ions

Consequent on the discovery of the saturation difficulties made in this section the data acquisition system, which was a digital system, has been changed to an analogue system for future experiments.
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5.2 Dissociative Ionization of N$_2$O by 60 Femtosecond Laser Pulses

In this section the results, analysis and discussion of intense laser field dissociative ionization of N$_2$O using 60 fs pulses at 750 nm are presented. The kinetic energies of the dissociative fragment ions and several dissociative ionization channels have been determined. The operating parameters appertaining to the femtosecond experiments on N$_2$O are listed in Table 5.7.

Table 5.7: The operating conditions for the data collected during the experiments on N$_2$O with 60 femtosecond laser pulses

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser repetition rate</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Laser wavelength</td>
<td>750 nm</td>
</tr>
<tr>
<td>Laser pulse duration</td>
<td>60 fs</td>
</tr>
<tr>
<td>Laser intensity range</td>
<td>$1.2 \times 10^{14} - 5.9 \times 10^{15}$ W/cm$^2$</td>
</tr>
<tr>
<td>Keldysh parameter</td>
<td>1.01 - 0.15</td>
</tr>
<tr>
<td>Extraction field range</td>
<td>75 - 600 V/cm</td>
</tr>
</tbody>
</table>

5.2.1 Results of the Dissociative Ionization of N$_2$O in a 60 Femtosecond Laser Field

Determination of the zero positions, as discussed in Section 2.8.1, allowed the higher energy TOF ion peaks to be designated as discussed in Section 2.8.1. TOF spectra recorded when the polarization was perpendicular and parallel to the TOF axis, are given in Figure 5.7.

In order to confirm that the kinetic energies associated with the features described are real, and not a function of the instrumentation, the positions of the peaks on the TOF axis of the spectra in relation to their zero positions were compared for different extraction fields. The initial kinetic energies of the ions for each extraction field were determined as for the picosecond data in Section 5.1.1. If the peaks have been properly determined the kinetic energy values should be the same for each extraction field, within the experimental error.
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Figure 5.7: TOF spectra of N$_2$O fragment ions resulting from dissociative ionization by 60 fs laser pulses at 750 nm, with a gas pressure of 1.5 x 10$^{-7}$ mbar, an extraction field of 300 V/cm and a laser intensity of 9 x 10$^{14}$ W/cm$^2$. The labels show the zero positions of the ions.

The initial kinetic energies of the fragment ions were determined from spectra, recorded with three different extraction fields, 150, 300 and 450 V/cm, in order that as many energy groups as possible were detected and well resolved. It was necessary to use a higher extraction field for the acquisition of femtosecond TOF spectra than for the picosecond TOF spectra since the ions dissociating in a femtosecond field have higher initial velocities. Also the TOF peaks were better defined in the femtosecond case and using higher extraction fields did not significantly decrease the detail on the spectrum but was advantageous in that it increased the collection efficiency of the detector.
Figure 5.8: The regions of the TOF spectra that include NO$^+$ and N$_2^+$ recorded with extraction fields of 150 V/cm, 300 V/cm and 450 V/cm. The laser polarization direction was parallel to the TOF axis. The laser intensity is $5.9 \times 10^{15}$ W/cm$^2$ and the ambient pressure $8 \times 10^8$ mbar.

Figure 5.8, shows the regions of the spectra including the NO$^+$ and N$_2^+$ ions and illustrates that there are two energy groups of NO$^+$ ions, A and B, resolvable in all three spectra. In the spectrum recorded with an extraction field of 150 V/cm there are two further peaks at 2.39 and 2.43 μs on either side of A. The energy of the ions in these peaks is 0.14 eV. The designation of this group is tentative since the peak heights reside only just outside the error of $\Delta N = N^{1/2}$ where N is the number
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of counts detected in the time bin of the MCS. The number of counts in the peak channel for the energy group A is 33, the trough between the peaks is 21 and the undetermined peak at 2.39 μs is 29. This possible energy group is not resolvable in the spectra recorded with the other two extraction fields. Using the analytical technique described in Section 2.8.1 the peak energies of the NO⁺ ion groups were calculated for three different extraction fields and are shown in Table 5.8.

Table 5.8: The NO⁺ energy groups deduced from spectra recorded with three different extraction fields.

<table>
<thead>
<tr>
<th>Extraction field (V/cm)</th>
<th>Energy Group, A (eV)</th>
<th>Energy Group, B (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0</td>
<td>2.17 ± 0.28</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>2.31 ± 0.58</td>
</tr>
<tr>
<td>450</td>
<td>0</td>
<td>2.03 ± 0.82</td>
</tr>
</tbody>
</table>

Frasinski et al, 1991, using 600 nm laser light of 600 fs pulse duration which produce a focused laser intensity of $1 \times 10^{15}$ W/cm² detected an ion energy group, equivalent to the NO⁺ energy group B in the present work, and measured the energy as 1.5-2.0 eV. The other energy group, A was not detected. The TOF spectra of N₂O taken from Frasinski et al, 1991, is given in Figure 5.9.

![Figure 5.9: Time of flight spectrum of the dissociative ionization of N₂O by 600 nm laser light of 600 fs pulse duration. The focused intensity was $1 \times 10^{15}$ W/cm² and the laser polarization direction was parallel to the TOF axis (Frasinski et al, 1991).](image)
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The other contributions to this part of the TOF spectra come from the N$_2^+$ peaks. The spectrum recorded with 150 V/cm extraction field shows three energy groups of N$_2^+$ ions, C and D, where C is a zero energy group and D is a finite energy group. The zero energy group, C, appears in all three spectra taken at different extraction fields, with an easily distinguished peak position. The peak due to the energy group D also appears in all three spectra; however, it is less certain due to low statistics. Table 5.9 shows the energy values deduced from the three spectra of different extraction voltages for the two energy groups associated with the N$_2^+$ ion. Frasinski et al, 1991, detected a peak corresponding to the N$_2^+$ ion, as shown in Figure 5.10, but did not quote an energy for this ion.

Table 5.9: The N$_2^+$ energy groups deduced from spectra recorded with three different extraction fields.

<table>
<thead>
<tr>
<th>Extraction field (V/cm)</th>
<th>Energy Group, C (eV)</th>
<th>Energy Group, D (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0</td>
<td>1.17 ± 0.14</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>1.89 ± 0.76</td>
</tr>
<tr>
<td>450</td>
<td>0</td>
<td>2.18 ± 0.88</td>
</tr>
</tbody>
</table>

Figure 5.10 shows the regions of the spectra containing the N$^+$ and O$^+$ ion peaks and shows how the peaks alter with changing extraction field. The peak values of the energy groups for the O$^+$ and N$^+$ ions are shown in Tables 5.10. The peak designation for the O$^+$ ions on the spectrum recorded with an extraction field of 150 V/cm is tentative, since the peak heights are within the error, N$^{1/2}$, where N is the number of ion counts in the peak channel. However, the peaks shown for the spectra recorded with 300 and 450 V/cm extraction fields are mostly outside the range of statistical fluctuation (shown as solid lines).

Figure 5.11 shows the regions of the spectra containing the N$^{2+}$, O$^{2+}$, N$^{3+}$, O$^{3+}$, N$^{4+}$ and O$^{4+}$ ion peaks. However, only O$^{2+}$, N$^{2+}$, O$^{3+}$ and N$^{3+}$ have been labeled due to the uncertainty in the quadruply ionized ions. This region of the spectrum is more complex due to the overlapping of the peaks from higher energy ions with shorter flight times. The energy groups for the O$^{2+}$, N$^{2+}$, O$^{3+}$ and N$^{3+}$ ions are given in Table 5.10.
Figure 5.10: The regions of the TOF spectra that include O⁺ and N⁺ recorded with extraction fields of 150 V/cm, 300 V/cm and 450 V/cm. The laser polarization direction is parallel to the TOF axis. The laser intensity is $5.9 \times 10^{15}$ W/cm² and the ambient pressure $8 \times 10^9$ mbar.
Figure 5.11: The regions of the TOF spectra that include \( O^{2+} \) to \( N^{4+} \) with extraction fields of 150 V/cm, 300 V/cm and 450 V/cm. The laser polarization direction is parallel to the TOF axis. The laser intensity is \( 5.9 \times 10^{15} \text{ Wcm}^2 \) and the ambient pressure \( 8 \times 10^{-9} \text{ mbar} \).
Table 5.10: The $O^+$, $N^+$, $O^{2+}$, $N^{2+}$, $O^{3+}$ and $N^{3+}$ energy groups from spectra recorded with three different extraction fields

<table>
<thead>
<tr>
<th>Ion</th>
<th>Extraction field (V/cm)</th>
<th>Energy Group, $E$ (eV)</th>
<th>Energy Group, $F$ (eV)</th>
<th>Energy Group, $G$ (eV)</th>
<th>Energy Group, $H$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O^+$</td>
<td>150 0</td>
<td>$1.69 \pm 0.32$</td>
<td>not resolved</td>
<td>$8.58 \pm 0.82$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300 0</td>
<td>$1.69 \pm 0.84$</td>
<td>$4.90 \pm 1.08$</td>
<td>$9.76 \pm 1.50$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>450 0</td>
<td>not resolved</td>
<td>$4.61 \pm 1.54$</td>
<td>$15.25 \pm 3.06$</td>
<td></td>
</tr>
<tr>
<td>$N^+$</td>
<td>150 0</td>
<td>$1.94 \pm 0.64$</td>
<td>$3.80 \pm 0.64$</td>
<td>$7.36 \pm 0.78$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300 0</td>
<td>$1.94 \pm 0.96$</td>
<td>$4.36 \pm 1.46$</td>
<td>$7.75 \pm 1.28$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>450 0</td>
<td>not resolved</td>
<td>$4.36 \pm 1.46$</td>
<td>$8.54 \pm 1.70$</td>
<td></td>
</tr>
<tr>
<td>$O^{2+}$</td>
<td>150 $24.47 \pm 2.56$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>300 $21.96 \pm 4.90$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>450 $21.96 \pm 7.32$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N^{2+}$</td>
<td>150 0</td>
<td>$22.38 \pm 2.94$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>300 0</td>
<td>$19.83 \pm 4.42$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>450 0</td>
<td>$21.09 \pm 12.12$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O^{3+}$</td>
<td>150 $44.07 \pm 5.60$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>300 $44.07 \pm 8.84$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>450 $49.41 \pm 15.22$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N^{3+}$</td>
<td>150 $8.54 \pm 1.72$</td>
<td>$56.46 \pm 7.18$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>300 $6.27 \pm 3.58$</td>
<td>$69.71 \pm 13.32$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>450 $6.27 \pm 6.26$</td>
<td>$76.85 \pm 15.22$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.2.2 Analysis of the Femtosecond Laser Results

The momenta for all the ion energy groups in the spectra were calculated and they have been used to try to determine which channels were open for the dissociative ionization of \( \text{N}_2\text{O} \) by summing the momenta of the participating ions to zero since the momentum of the molecular system is conserved. The results of this investigation are shown in Table 5.11. The FWMH for the momenta calculated from the FWHM of the ion peaks are shown in the table. Although there is structure apparent in the \( \text{N}^+ \) and \( \text{O}^+ \) ion peaks the FWHM of the overall \( \text{N}^+ \) distribution is \( 3.60 \times 10^{-22} \) (Jkg)\(^{1/2} \) and the overall FWHM for the \( \text{O}^+ \) distribution is \( 5.08 \times 10^{-22} \) (Jkg)\(^{1/2} \).

Table 5.11: Tentative determination of the dissociative ionization channels of \( \text{N}_2\text{O} \) in an intense 60 fs duration laser field.

<table>
<thead>
<tr>
<th>Ion fragment (Energy group)</th>
<th>Peak of the kinetic energy distribution (eV)</th>
<th>Momentum x10(^{-22}) (Jkg)(^{1/2})</th>
<th>FWHM of the momentum distribution (x10(^{-22}) (Jkg)(^{1/2}))</th>
<th>Proposed Channel</th>
<th>Total Measured energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}^+ ) (I)</td>
<td>0</td>
<td>0</td>
<td>--</td>
<td>( \text{NO} + \text{N}^+ )</td>
<td>0</td>
</tr>
<tr>
<td>( \text{NO}^+ ) (A)</td>
<td>0</td>
<td>0</td>
<td>0.96</td>
<td>( \text{NO}^+ + \text{N} )</td>
<td>0</td>
</tr>
<tr>
<td>( \text{N}_2^+ ) (C)</td>
<td>0</td>
<td>0</td>
<td>0.72</td>
<td>( \text{N}_2^+ + \text{O} )</td>
<td>0</td>
</tr>
<tr>
<td>( \text{O}^+ ) (E)</td>
<td>0</td>
<td>0</td>
<td>--</td>
<td>( \text{N}_2 + \text{O}^+ )</td>
<td>0</td>
</tr>
<tr>
<td>( \text{NO}^+ ) (B)</td>
<td>2.17 ± 0.28</td>
<td>1.86 ± 0.24</td>
<td>0.96</td>
<td>( \text{NO}^+ + \text{N}^+ )</td>
<td>5.97 ± 0.74</td>
</tr>
<tr>
<td>( \text{N}^+ ) (K)</td>
<td>3.80 ± 0.68</td>
<td>1.66 ± 0.30</td>
<td>--</td>
<td>( \text{N}_2 + \text{N}^+ )</td>
<td>5.51 ± 1.09</td>
</tr>
<tr>
<td>( \text{N}_2^+ ) (D)</td>
<td>1.17 ± 0.14</td>
<td>1.32 ± 0.16</td>
<td>--</td>
<td>( \text{N}_2^+ + \text{O}^+ )</td>
<td>3.63 ± 0.72</td>
</tr>
<tr>
<td>( \text{O}^+ ) (G)</td>
<td>4.90 ± 1.08</td>
<td>2.04 ± 0.45</td>
<td>--</td>
<td>( \text{N}^+ + \text{N} + \text{O}^+ )</td>
<td>15.94 ± 1.15</td>
</tr>
<tr>
<td>( \text{N}^+ ) (A)</td>
<td>1.94 ± 0.64</td>
<td>1.20 ± 0.40</td>
<td>--</td>
<td>( \text{N}^+ + \text{N}^+ + \text{O}^+ )</td>
<td>46.85 ± 3.90</td>
</tr>
<tr>
<td>( \text{O}^+ ) (F)</td>
<td>1.69 ± 0.32</td>
<td>1.20 ± 0.23</td>
<td>--</td>
<td>( \text{N}^+ + \text{N}^+ + \text{O}^+ )</td>
<td>109.07 ± 9.27</td>
</tr>
<tr>
<td>( \text{N}^+ ) (I)</td>
<td>0</td>
<td>0</td>
<td>--</td>
<td>( \text{N}^+ + \text{N}^+ + \text{O}^+ )</td>
<td>0</td>
</tr>
<tr>
<td>( \text{O}^+ ) (H)</td>
<td>8.58 ± 0.84</td>
<td>2.70 ± 0.26</td>
<td>--</td>
<td>( \text{N}^+ + \text{N}^+ + \text{O}^+ )</td>
<td>0</td>
</tr>
<tr>
<td>( \text{N}^+ ) (O)</td>
<td>22.38 ± 2.94</td>
<td>4.08 ± 0.54</td>
<td>4.80</td>
<td>( \text{N}^+ + \text{N}^+ + \text{O}^+ )</td>
<td>46.85 ± 3.90</td>
</tr>
<tr>
<td>( \text{N}^+ ) (M)</td>
<td>24.47 ± 2.56</td>
<td>4.56 ± 0.48</td>
<td>--</td>
<td>( \text{N}^+ + \text{N}^+ + \text{O}^+ )</td>
<td>109.07 ± 9.27</td>
</tr>
<tr>
<td>( \text{N}^+ ) (Q)</td>
<td>5.64 ± 7.18</td>
<td>6.48 ± 0.83</td>
<td>--</td>
<td>( \text{N}^+ + \text{N}^+ + \text{O}^+ )</td>
<td>109.07 ± 9.27</td>
</tr>
<tr>
<td>( \text{N}^+ ) (S)</td>
<td>8.54 ± 1.72</td>
<td>2.52 ± 0.51</td>
<td>--</td>
<td>( \text{N}^+ + \text{N}^+ + \text{O}^+ )</td>
<td>109.07 ± 9.27</td>
</tr>
<tr>
<td>( \text{O}^+ ) (S)</td>
<td>44.07 ± 5.60</td>
<td>6.12 ± 0.78</td>
<td>--</td>
<td>( \text{N}^+ + \text{N}^+ + \text{O}^+ )</td>
<td>109.07 ± 9.27</td>
</tr>
</tbody>
</table>
It was not possible to determine a FWHM of the momenta distributions for the majority of the singly charged ions since the ion peaks for the different energy groups merged into one another. The FWHM for the $N_2^+$ ($D$) is not stated due to the low statistics of the ion peak. The channels $\text{NO}^+ + N$, $N_2^+ + O$, $\text{NO} + N^+$ and $N_2 + O^+$ are not momenta matched since the experimental apparatus was not equipped to detect neutral fragments. They are not Coulomb explosions and the total kinetic energy released for these channels will be low. The zero energy groups of $\text{NO}^+$, $N^+$, $O^+$ and $N_2^+$ were probably produced from these channels. The momenta for the $\text{NO}^+ + N^+$ channel do equate within the limits of the experimental errors, but the momenta matching for the $N_2^+ + O^+$ channel does not equate even considering the error limits. This is probably due to the peak of the $O^+$ ($G$) not being the exact arrival time for ions from this channel, since there is significant overlap of the oxygen ion energy groups.

The momenta of the ion fragments of the $N^+ + N^+ + O^+$ channel do not exactly equate, with the oxygen ion having the greater momenta. This is probably due to the central nitrogen ion momenta being greater than zero. Since the process is a Coulomb explosion into a symmetric channel and the central nitrogen does not lie on the centre of mass of the molecule, the central nitrogen is expected to have a small finite energy. It is possible that this ion group will be small and so will appear in the 0 eV energy group indistinguishable from the $N^+$ signal from the $N^+ + \text{NO}$ channel. Low kinetic energies for the central nitrogen ions should be expected for the $N_2^+$ signal from the $N^2+ + N^2+ + O^{2+}$ and the $N^{3+} + N^{3+} + O^{3+}$ channels. The mismatch of the momenta of the terminal ions for the $N^{3+} + N^{3+} + O^{3+}$ channel suggests that the central nitrogen moves away in the direction of the oxygen. This cannot be the case for a symmetrically charged channel like this and it is thought that the true energy value for this channel resides within the energy distribution of the $N^{3+}$ and/or $O^{3+}$ ions.

Luk et al, 1992, found that during the dissociative ionization of $N_2O$, by 248 nm wavelength light with a laser pulse duration of 600 fs, the terminal ions were more easily ionized than the central ions. The only evidence for this in the present work is the $N^+ + N + O^+$ channel.
Chapter 5

Table 5.12: The calculated critical distance using each channel as a separate calculation

<table>
<thead>
<tr>
<th>Channel</th>
<th>Calculated Coulomb energy, $E_C$ (eV)</th>
<th>Experimentally determined energy, $E_M$ (eV)</th>
<th>Energy Ratio $\left(\frac{E_M}{E_C}\times100\right)$</th>
<th>Mean inter-nuclear separation, $r$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$^+$ + N$^+$</td>
<td>8.37</td>
<td>5.97 ± 0.74</td>
<td>71.3</td>
<td>1.61</td>
</tr>
<tr>
<td>$N_2^+$ + O$^+$</td>
<td>8.23</td>
<td>5.51 ± 1.09</td>
<td>67.0</td>
<td>1.74</td>
</tr>
<tr>
<td>N$^+$ + N + O$^+$</td>
<td>6.22</td>
<td>3.63 ± 0.72</td>
<td>58.4</td>
<td>1.98</td>
</tr>
<tr>
<td>N$^+$ + N$^+$ + O$^+$</td>
<td>31.13</td>
<td>15.94 ± 1.15</td>
<td>51.2</td>
<td>2.26</td>
</tr>
<tr>
<td>$N^2$$^+$ + N$^2$$^+$ + O$^2$$^+$</td>
<td>124.53</td>
<td>46.85 ± 3.90</td>
<td>37.6</td>
<td>3.07</td>
</tr>
<tr>
<td>N$^{+}$ + N$^{+}$ + O$^{+}$</td>
<td>280.17</td>
<td>109.07 ± 9.27</td>
<td>38.9</td>
<td>2.97</td>
</tr>
</tbody>
</table>

5.2.3 Discussion of the Femtosecond Laser Results

The calculated internuclear separations from which the Coulomb explosions take place are given in Table 5.12. It was assumed that the ratio of the $N_2$-O and $N_2$-N$_4$ bond was maintained even after the molecule had expanded. In this case the total energy and charges of the fragment ions were known and the mean internuclear separation, $r$, was calculated from Equations 5.2, 5.3 and 5.4 and are shown in Table 5.12.

These simple calculations, the results of which are shown in Table 5.12, show what the percentage the experimentally determined energy is of the calculated Coulomb explosion energy for all channels. Frasinski et al, 1991, found that the experimental to calculated energy ratio for the NO$^+$ + N$^+$ channel was 65.7 % (taking the midpoint of their energy distributions for the two ions) and for the N$^2$$^+$ + N$^2$$^+$ + O$^2$$^+$ the ratio was 30.2% which compares relatively well with the results in this section. The average percentage for all the channels found in this Section is 54.1 ± 14.1 % and the average value of the mean internuclear separation is 2.3 Å.
Chapter 5

5.2.4 Conclusion

Coulomb explosions have been found to occur in a femtosecond laser field with energies that appear to suggest that the critical distance changes for different channels. The internuclear separation does not decrease slightly as found for diatomic molecules (Seideman et al, 1995a and references therein) but increase by 126% from lowest internuclear separation to the highest. This could be due to the fact that the Coulomb explosions have been assumed to be taking place when the molecule is linear. It is not unreasonable to suggest that the field could modify the geometry of the molecule, as shown in CO$_2$ (Chapter 6) and SO$_2$ (Cornaggia et al, 1996b) such that bends are induced.

5.3 Comparisons of Laser Dissociation by Pulses of Picosecond and Femtosecond Pulse Duration

There is no direct comparison between the two spectra shown in Figure 5.12 since they were collected with different extraction fields and were produced by different laser intensities. The femtosecond spectrum was produced by the highest laser intensity using the femtosecond laser and the picosecond spectrum by the highest intensity using the picosecond laser. There is a distinct similarity between the shapes of the peaks on the spectra shown in Figure 5.12, but there is more detail to the femtosecond spectra. Another difference is that the highest stage of ionization detected were quadruply charged ions for the femtosecond spectrum compared to doubly charged ions for the picosecond spectrum. This is due to the higher intensity using the femtosecond laser compared to the picosecond laser.
Chapter 5

Figure 5.12: Spectra of the dissociative ionization of N₂O by 532 nm laser light of 35 ps pulse duration with a focused laser intensity of 1.5 x 10¹⁴ W/cm² and by 750 nm laser light of 60 fs pulse duration with a focused laser intensity of 5.9 x 10¹⁵ W/cm². The laser polarization direction was perpendicular to the TOF axis for both spectra.

Comparison of the spectra recorded using both femtosecond and picosecond pulses where the laser polarization direction is parallel to the TOF axis (see Figure 5.13) reveals that the different energy groups are much better resolved in the femtosecond laser spectrum than for the picosecond laser spectrum. The channels which were opened during the femtosecond laser pulse interactions have been found to be predominantly Coulomb explosion channels from an internuclear separation that was larger than the equilibrium internuclear separations for the molecule. The channels which were opened during the picosecond laser pulse interactions produce kinetic energies too low to be attributed to Coulomb explosion.
**Chapter 5**

![Graph 1: 532 nm laser light of 35 ps pulse duration](image1.png)

**Graph 1:** Spectra of the dissociative ionization of $N_2O$ by 532 nm laser light of 35 ps pulse duration with a focused laser intensity of $1.5 \times 10^{14}$ W/cm$^2$ and by 750 nm laser light of 60 fs pulse duration with a focused laser intensity of $5.9 \times 10^{15}$ W/cm$^2$. The polarization direction is parallel to the TOF axis for both spectra.

**Figure 5.13:** Spectra of the dissociative ionization of $N_2O$ by 532 nm laser light of 35 ps pulse duration with a focused laser intensity of $1.5 \times 10^{14}$ W/cm$^2$ and by 750 nm laser light of 60 fs pulse duration with a focused laser intensity of $5.9 \times 10^{15}$ W/cm$^2$. The polarization direction is parallel to the TOF axis for both spectra.

**5.4 Summary**

This chapter has presented results for the dissociative ionization of nitrous oxide by 750 nm laser light of 60 fs pulse duration and also 532 nm laser light of 35 ps pulse duration. There was evidence of only one Coulomb explosion channel for the picosecond interactions. The majority of channels involved dissociative ionization followed by post dissociative ionization. The results from the femtosecond laser spectra showed that there was a significant amount of Coulomb explosions of the dissociating molecules. The internuclear separation of the atoms/ions at Coulomb explosion was calculated and found to increase with increasing channel order.
Chapter 6: Dissociative Ionization of Carbon Dioxide in Intense Femtosecond Laser Fields

6.0 Introduction

This chapter describes an investigation of the dissociative ionization of carbon dioxide by an intense laser field of 60 femtosecond pulse duration. The measurement of the TOF of the ionic fragments leads to the calculation of the initial kinetic energies of the fragments and a determination of several dissociative ionization channels. Also included are angular measurements of the initial trajectories of CO$_2$ molecules dissociatively ionizing in a femtosecond laser field. Finally, the first results of femtosecond laser pulse induced dissociation of CO$_2$ molecules from vibrationally excited states are presented.

Carbon dioxide is a triatomic molecule (O-C-O) of linear symmetry with equilibrium bond lengths (C-O) of 1.163 Å (Douglas and Moller, 1954). The ground vibrational state, (000), is a symmetric mode which has a zero permanent dipole moment. The ground vibrational state is a bend mode with a most probable bend angle of 174° (Herzberg, 1966).
Chapter 6

6.1 Vibrational Population through Thermal Excitation

Collisions between a test gas and a heated surface result in energy being transferred from one to the other. This can result in the vibrational excitation of the molecule to which the energy is transferred; the process being termed collisional excitation. Equation 6.1 can be used to determine the mean temperature of the molecules within the heated surface.

\[ E = \frac{3}{2} kT \]  
Equation 6.1

Where \( E \) is the mean thermal energy of the molecules, \( k \) is the Boltzmann constant and \( T \) is the temperature of the molecules. At 473 K, which is the temperature used in the experiments described in Section 6.4, \( E \), the peak of a Boltzmann distribution of energies, occurs at 61.2 meV. Calculations have shown that 26% of the molecules in this distribution have thermal energies greater than 83 meV, which is the energy of the first vibrationally excited state of carbon dioxide, a bending mode (010) (Johnstone et al., 1993). Table 6.1 shows the percentages of molecules in higher vibrationally excited states when the temperature of the exciting molecules is 473 K, which have been calculated from the population densities found from Equation 6.2.

\[ p_v = \frac{g_v e^{\frac{\Delta E_v}{kT}}}{\sum_{v=0} g_v e^{\frac{\Delta E_v}{kT}}} \]  
Equation 6.2

where \( p_v \) is the population fraction of the vibrational level, \( g_v \) is the statistical weight \( \Delta E_v \) is the energy of the level above the ground state and \( T \) is the temperature of the gas.

The first vibrationally excited state (010) is a bend mode and excitation of CO\(_2\) to the (010) mode results in the central carbon atom oscillating in a direction perpendicular to the C\(_n\) axis, as shown in Figure 6.1, giving a minimum O-C-O bond angle, \( \gamma \), of 156° (Tennyson and Newell, 1998).
Chapter 6

Table 6.1: The first four vibrationally excited states of CO$_2$ in the electronic ground state where $\nu$ is the vibrational state, $g_\nu$ is the statistical weight of the state, $E$ is the energy above the ground state and $P_\nu$ is the percentage of molecules in this state at 473 K

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$g_\nu$</th>
<th>Mode</th>
<th>$E$ (meV)</th>
<th>$P_\nu$ at 473 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>000</td>
<td>0.00</td>
<td>74.28</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>010</td>
<td>82.75</td>
<td>19.43</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>020</td>
<td>159.37</td>
<td>1.51</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>020</td>
<td>165.54</td>
<td>2.54</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>100</td>
<td>172.11</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Figure 6.1: The vibrationally excited bend mode (010) of CO$_2$. The movement of the oxygen atom during the bend is perpendicular to the C$_n$ axis (towards and away from the oxygen atoms).

6.2 Dissociative Ionization of CO$_2$ by a 60 Femtosecond Laser Field

This section includes results and analysis of the dissociative ionization of carbon dioxide when subjected to an intense 750 nm laser field of 60 fs pulse duration. The kinetic energies of the fragment ions are reported and several dissociation channels determined.
Chapter 6

6.2.1 Spectra of the Dissociative Ionization of CO$_2$ by a 60 fs Laser Field

Table 6.2: The operating conditions for the data collected during the experiments on CO$_2$ with 60 fs femtosecond laser pulses

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser repetition rate</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Laser wavelength</td>
<td>750 nm</td>
</tr>
<tr>
<td>Laser pulse duration</td>
<td>60 fs</td>
</tr>
<tr>
<td>Laser intensity range</td>
<td>$5 \times 10^{15}$ W/cm$^2$</td>
</tr>
<tr>
<td>Keldysh parameter</td>
<td>0.16</td>
</tr>
<tr>
<td>Extraction field range</td>
<td>300 V/cm</td>
</tr>
</tbody>
</table>

Figure 6.2 shows spectra recorded with laser polarization parallel and perpendicular to the TOF axis. The ion peaks in the TOF spectra recorded when the laser polarization direction was perpendicular to the TOF axis were used to determine the 'zero positions' of the ions, as discussed in Section 2.8.1.

Significant differences can be seen between the spectra recorded when the laser polarization direction was parallel and perpendicular to the TOF axis. The number of oxygen ions detected for all stages of ionization compared to the number of carbon ions has increased for the spectrum recorded with the laser polarization perpendicular to the TOF axis. Also, there appears to be one smooth energy distribution for each ion for the spectra recorded with the laser polarization direction perpendicular to the TOF axis, yet for the spectra recorded for the laser polarization parallel to the TOF axis more than one ion peak for each species is distinguishable for the CO$^+$, O$^+$, O$^{2+}$ and O$^{3+}$ ions. The carbon ions, for all stages of ionization, produce only one ion peak for spectra recorded with both laser polarization directions.
Figure 6.2: TOF spectra of CO$_2$ fragment ions resulting from the dissociative ionization by 60 fs laser pulses with a laser intensity of $5 \times 10^{15}$ W/cm$^2$ and recorded with an extraction field of 300 V/cm.

6.2.2 Determination of the Fragment Ion Kinetic Energies and the Dissociative Ionization Channels

The kinetic energies of the fragment ions from the dissociative ionization of CO$_2$ were calculated as described in Section 2.5 and shown in Sections 5.1.1 and 5.2.1 for N$_2$O. Figure 6.3 shows the kinetic energy distributions found from the 1-D TOF spectra for the fragment ions from CO$_2$. The peak momenta and FWHM of the momenta for these ions are given in Table 6.3.
Figure 6.3: The kinetic energy distributions, calculated from a 1-D TOF spectrum, for the fragment ions from the dissociative ionization of CO\(_2\) in a 60 fs laser field.
**Chapter 6**

The energies determined from the 1D-TOF spectrum of CO$_2$ are given in Table 6.3, as well as the proposed dissociative ionization channels. The determination of the channels for this molecule is much more difficult using a 1D-TOF spectra for CO$_2$ than for N$_2$O due to the symmetry of the molecule. In the case of N$_2$O the terminal ions are different species producing two different ions with the same momenta but different kinetic energies.

**Table 6.3: Tentative determination of the dissociation channels of CO$_2$ in a 60 fs laser field.**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Peak kinetic energy (eV)</th>
<th>FWHM of kinetic energy distribution (eV)</th>
<th>Peak of momenta ($\frac{\sqrt{2}}{2} M_0 v^2$)</th>
<th>FWHM of momenta distribution $\times 10^{-22}$ ($\frac{\sqrt{2}}{2} M_0 v^2$)</th>
<th>Proposed channel</th>
<th>Total experimentally determined kinetic energy for channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$^+$</td>
<td>0</td>
<td>0.25</td>
<td>0</td>
<td>0.61</td>
<td>CO$^+$ + O</td>
<td>0</td>
</tr>
<tr>
<td>O$^+$</td>
<td>0</td>
<td>0.4</td>
<td>0</td>
<td>0.58</td>
<td>CO + O$^+$</td>
<td>0</td>
</tr>
<tr>
<td>CO$^+$</td>
<td>1.5</td>
<td>2.5</td>
<td>1.49</td>
<td>1.41</td>
<td>CO$^+$ + O$^+$</td>
<td>4.5</td>
</tr>
<tr>
<td>O$^+$</td>
<td>3</td>
<td>--</td>
<td>1.60</td>
<td>--</td>
<td>O$^+$ + C$^+$ + O$^+$</td>
<td>18</td>
</tr>
<tr>
<td>C$^+$</td>
<td>0</td>
<td>2.0</td>
<td>0</td>
<td>1.13</td>
<td>C$^+$ + O$^+$</td>
<td>14</td>
</tr>
<tr>
<td>C$^{2+}$</td>
<td>22</td>
<td>30</td>
<td>4.32</td>
<td>3.17</td>
<td>O$^{2+}$ + C$^+$ + O$^{2+}$</td>
<td>44</td>
</tr>
<tr>
<td>O$^{2+}$</td>
<td>35</td>
<td>--</td>
<td>5.45</td>
<td>--</td>
<td>O$^{2+}$ + C$^{2+}$ + O$^{2+}$</td>
<td>70</td>
</tr>
<tr>
<td>C$^{3+}$</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>1.38</td>
<td>C$^{3+}$ + O$^{3+}$</td>
<td>100</td>
</tr>
<tr>
<td>O$^{3+}$</td>
<td>50</td>
<td>40</td>
<td>6.52</td>
<td>2.66</td>
<td>O$^{3+}$ + C$^{3+}$ + O$^{3+}$</td>
<td>130</td>
</tr>
<tr>
<td>C$^{4+}$</td>
<td>0</td>
<td>5.5</td>
<td>0</td>
<td>1.97</td>
<td>C$^{4+}$ + O$^{4+}$</td>
<td>140</td>
</tr>
</tbody>
</table>

It is impossible to say with any degree of certainty when studying a 1D-TOF of CO$_2$ whether symmetric channels are occurring or not. It is necessary to compare the energies of the channels with those determined from covariance mapping techniques by other research groups. The energies of the channels given in Table 6.4 compare well with channel energies determined by Frasinski et al, 1994 and Cornaggia et al, 1994, both of whom used covariance mapping. Not all of the channels determined using covariance mapping (Frasinski et al, 1994 and Cornaggia et al, 1994) have been found using 1D-TOF analysis since only the peaks of the kinetic energy distributions can be analyzed using the 1-D technique. Some of the ion distributions may result from ions produced by different dissociating channels with initial energies similar but not quite the same as each other.
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Table 6.4: The total kinetic energies of the fragment ions produced from the dissociative ionization channels of CO₂.

<table>
<thead>
<tr>
<th>Channel</th>
<th>Total kinetic energy of channel (eV) (Present work)</th>
<th>Energy ratio(%) $E_a/E_c \times 100$ (Present work)</th>
<th>Internuclear separation at Coulomb explosion (Å)</th>
<th>Total kinetic energy of channel (eV) (Frasinski et al, 1994)</th>
<th>Total kinetic energy of channel (eV) (Cornaggia et al, 1994)</th>
<th>Energy ratio(%) $E_a/E_c \times 100$ (Cornaggia et al, 1994)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO⁺ + O⁺</td>
<td>4.5</td>
<td>54.4</td>
<td>2.13</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O⁺ + C⁺ + O⁺</td>
<td>18</td>
<td>58.2</td>
<td>2.0</td>
<td>10-24</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O⁺ + C⁺⁺ + O⁺</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O⁺ + C⁺⁺ + O⁺⁺</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>22-44</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O₂⁺ + C⁺ + O⁺⁺</td>
<td>44</td>
<td>59.3</td>
<td>1.96</td>
<td>36-48</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O₂⁺ + C⁺⁺ + O⁺⁺</td>
<td>70</td>
<td>56.6</td>
<td>2.06</td>
<td>56-76</td>
<td>62</td>
<td>50</td>
</tr>
<tr>
<td>O₂⁺ + C⁺⁺ + O⁺⁺</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>80-100</td>
<td>92</td>
<td>57</td>
</tr>
<tr>
<td>O₃⁺ + C⁺⁺ + O⁺⁺</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>87</td>
<td>50</td>
</tr>
<tr>
<td>O₃⁺ + C⁺⁺ + O⁺⁺</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>223</td>
<td>45</td>
<td>—</td>
</tr>
<tr>
<td>O₃⁺ + C⁺⁺ + O⁺⁺</td>
<td>100</td>
<td>35.9</td>
<td>3.24</td>
<td>90-130</td>
<td>130</td>
<td>47</td>
</tr>
</tbody>
</table>

The mean ratio of experimentally determined energy to the calculated Coulomb explosion energy from the equilibrium separation for the channels determined for the present work is 52.9 +/- 9.7 % compared to the mean of 49.8 +/- 20.7 % found from Cornaggia et al, 1994. The mean critical distance calculated from the kinetic energies of the five Coulomb explosion channels is 2.3 ± 0.5 Å.

6.2.3 Conclusion of the Femtosecond Laser Results

The present results for the kinetic energies of the peaks and the channel determination, given in Table 6.3, agree relatively well with Frasinski et al, 1994 and Cornaggia et al, 1994. However, it is clear that for a symmetric molecule such as CO₂ the use of covariance mapping is not just useful but necessary in the channel determination. The mean critical distance found for the channels of dissociative ionization of CO₂ is 2.3 ± 0.5 Å.
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6.3 Angular Investigations of the Dissociative Ionization of CO$_2$ in a Femtosecond Laser Field

This section contains the angular measurements of the initial trajectories of fragmentation ions produced in the interactions with 60 fs laser pulses at 750 nm with CO$_2$. The distributions of the ion trajectories dramatically show the bent nature of the dissociating molecules and allow the determination of the alignment functions for several dissociation channels.

6.3.1 Operating Parameters and Apparatus Arrangement

The optics used to manipulate the beam into the vacuum chamber have been described in Section 3.4.8. The arrangement of the TOF mass spectrometer and gas injection apparatus in the vacuum chamber has been described in Section 2.1.2. Adjustment of the laser polarization direction with respect to the TOF axis has been described in Section 3.3.6. A 2 mm diameter aperture was placed directly in front of the micro-channel plates. This was required in order that the angular resolution of the TOF mass spectrometer was improved.

Spectra were recorded at laser polarization direction increments of 5 degrees over a range of angles; -33 to +97 degrees, where 0° is defined as the direction parallel to the TOF axis. In order to prevent any systematic effects due to small drifts in intensity (±5% within the gating range) spectra for different polarization directions were taken in a random sequence. Analysis of the data involved summing the ion counts for the ion distribution for the different dissociative ionization channels for each spectrum. The number of counts for each ion were plotted for spectra recorded at each different polarization on a polar plot. The significance of the polar plots is that they show the number of ions dissociating along each angular trajectory with respect to the laser polarization direction. The operating parameters appertaining to the experiments to directly measure the angular distributions of the ions from the dissociative ionization of CO$_2$ are listed in Table 6.5.
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Table 6.5: The operating parameters for the data collected during experiments to determine the angular distributions of CO₂ fragments.

<table>
<thead>
<tr>
<th>Operating parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser repetition rate</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Laser wavelength</td>
<td>750 nm</td>
</tr>
<tr>
<td>Laser pulse width</td>
<td>60 fs</td>
</tr>
<tr>
<td>Laser intensity</td>
<td>7 x 10¹⁹ W/cm²</td>
</tr>
<tr>
<td>Keldysh parameter</td>
<td>0.14</td>
</tr>
<tr>
<td>Extraction field</td>
<td>500 V/cm</td>
</tr>
</tbody>
</table>

The channels for the dissociative ionization of CO₂ in the femtosecond laser field were taken from a covariance map. The technique, recently developed in the laboratory by another researcher will be presented in his thesis (Bryan, 2000). This map was used solely to determine the exact regions of the spectra to which ions from specific channels had contributed. Figure 6.4 shows the covariance map used for this purpose and Table 6.6 shows the range of energies found for the channels (Bryan et al, 1999) from the covariance map.

![Covariance Map](image)

**Figure 6.4**: Covariance map from which the energy ranges of the ions from dissociative ionization channels have been determined (Bryan et al, 1999).
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Table 6.6: FWHM of the energy distributions found from the covariance map for each of the islands shown in Figure 6.3 and from Frasinski et al, 1994.

<table>
<thead>
<tr>
<th>Island on Figure 6.3</th>
<th>Ion</th>
<th>Peak of ion energy distribution (eV) (present work)</th>
<th>Range of the FWHM of the ion energy distribution (eV) (present work)</th>
<th>Peak energy of ions (eV) (Frasinski et al, 1994)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O+</td>
<td>9</td>
<td>1.6-23</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>C+</td>
<td>0</td>
<td>0-1.5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>O+</td>
<td>16</td>
<td>6-30</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>O2+</td>
<td>22</td>
<td>6.5-35</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>O+</td>
<td>16</td>
<td>6-30</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>C2+</td>
<td>0</td>
<td>0-2.2</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>O2+</td>
<td>21</td>
<td>9-36</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>C+</td>
<td>0</td>
<td>0-0.7</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>O2+</td>
<td>35</td>
<td>22-52</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>C2+</td>
<td>0</td>
<td>0-2.5</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>O2+</td>
<td>40</td>
<td>30-60</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>O3+</td>
<td>49</td>
<td>33-68</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>O2+</td>
<td>37</td>
<td>28-55</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>C3+</td>
<td>0</td>
<td>0-3.4</td>
<td>---</td>
</tr>
<tr>
<td>8</td>
<td>O3+</td>
<td>58</td>
<td>40-80</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>C3+</td>
<td>0</td>
<td>0-3.4</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>O3+</td>
<td>49</td>
<td>---</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>C3+</td>
<td>0</td>
<td>---</td>
<td>0.5</td>
</tr>
</tbody>
</table>

6.3.2 Angular distributions of the fragment ions of CO$_2$

The angular resolution of the apparatus for ions with a specific initial kinetic energy can be determined as explained in Section 2.5 using the program shown in Appendix 3. Figure 6.5 shows the calculated angular resolutions for O$, O^{2+}$ and C$^+$ for an extraction field of 500 V/cm. The figure illustrates that angular resolution is lost as the kinetic energy of the ions approaches zero.
Figure 6.5 Angular resolution of \( C^+ \), \( O^+ \) and \( O^{2+} \) ions in a 500 V/cm extraction field.

Figure 6.6 Polar plots, as a function of the laser polarization direction, of \( CO^+ \) (thermal and energetic), \( C^+ \), \( O^+ \) from channels (1,1,1) and (1,2,1), \( C^{2+} \), and \( O^{2+} \) from channels (2,2,2) and (2,3,2) where \( r \) is the number of counts per laser pulse for each ion group. All data points are reflected into each quadrant.
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Figure 6.6 shows polar plots for some of the ions detected, when the laser and apparatus were operating under the conditions described in Section 6.3.1. The laser polarization direction is along the horizontal axis of the polar plots in Figure 6.6. The data points have been reflected into each quadrant for clarity. Quite strikingly, the trajectories of the majority of energetic carbon ions are perpendicular to the laser polarization direction and the majority of the trajectories of the energetic oxygen ions are along the laser field polarization direction.

6.3.3 Analysis of the Angular Distributions of Fragment ions of CO₂

Figure 6.6 showed that the oxygen ions had a larger velocity component along the laser polarization direction than orthogonal to it. This verifies that there is some degree of alignment of the CO₂ molecule along the laser polarization direction.

![Graphs showing angular distributions of ions](image)

*Figure 6.7: Angular distributions of fast O⁺ channels (1,1,1) and (1,2,1) and O²⁺ channels (2,2,2) and (2,3,2). The angle (theta) is the angle between the TOF axis and the laser polarization direction.*
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The present work also shows that for the energetic carbon ions the velocity component in the direction perpendicular to the TOF axis is much larger than parallel to it. In order for the carbon ion to have any velocity greater than that of thermal motion it must move out of its centralized position in the molecule.

Figure 6.7 shows the angular distributions of the O\(^+\) ions from the O\(^+\) + C\(^+\) + O\(^+\) and O\(^+\) + C\(^{2+}\) + O\(^+\) channels and the O\(^{2+}\) ions from the O\(^{2+}\) + C\(^{2+}\) + O\(^{2+}\) and O\(^{2+}\) + C\(^{3+}\) + O\(^{2+}\) channels. An Acos\(^n\)\(\theta\) distribution has been fitted to the angular distributions shown in Figure 6.7. This form of distribution has been used previously by Dietrich et al, 1993 and Safvan et al, 1996. There is no special physical significance for this type of distribution but its continuous functional form make it more physical than the triangular distribution, used by Cornaggia, 1996b. Table 6.7 shows the least square fit Acos\(^n\)\(\theta\) distributions for channels (1,1,1), (1,2,1), (2,2,2) and (2,3,2).

Table 6.7: Parameters from least square fits of Acos\(^n\)\(\theta\) to the angular distributions of the oxygen ions produced in the dissociative ionization of CO\(_2\) in the femtosecond laser field.

<table>
<thead>
<tr>
<th>Channel</th>
<th>n</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,1,1)</td>
<td>12</td>
<td>0.0028</td>
</tr>
<tr>
<td>(1,2,1)</td>
<td>13</td>
<td>0.0002</td>
</tr>
<tr>
<td>(2,2,2)</td>
<td>15</td>
<td>0.0017</td>
</tr>
<tr>
<td>(2,3,2)</td>
<td>16</td>
<td>0.0014</td>
</tr>
</tbody>
</table>

The apparent structure of the ion distributions given in Figure 6.6 is not attributed to pendular motion (Friedrich and Herschbach, 1996 and Kumar et al, 1996) but is simply scatter. Table 6.8 shows the n values determined by Dietrich et al, 1993, for iodine using a 625 nm laser with a pulse duration of 80 fs.

Table 6.8: List of fragmentation channels for the angular distributions of iodine. The n parameters are from the Acos\(^n\)\(\theta\) distributions that were fitted to the data. (Dietrich et al, 1993)

<table>
<thead>
<tr>
<th>Channel</th>
<th>Intensity (W/cm(^2))</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>I(^+) + I(^+)</td>
<td>1 x 10(^{14})</td>
<td>3.10 ± 0.23</td>
</tr>
<tr>
<td>I(^{2+}) + I(^+)</td>
<td>1.8 x 10(^{14})</td>
<td>4.28 ± 0.25</td>
</tr>
<tr>
<td>I(^{2+}) + I(^{2+})</td>
<td>3.7 x 10(^{14})</td>
<td>6.11 ± 0.46</td>
</tr>
<tr>
<td>I(^{3+}) + I(^+)</td>
<td>3.7 x 10(^{14})</td>
<td>7.11 ± 0.36</td>
</tr>
</tbody>
</table>
Table 6.8 shows that the fitting parameters, n, for iodine (Dietrich et al, 1993) are all lower than any observed in the present work. This can be explained since CO$_2$ is lighter than I$_2$ and will, therefore, be more strongly aligned during the laser pulse.

Figure 6.7 shows a striking feature that appears more clearly on this plot than on the corresponding polar plot, given in Figure 6.6. Although the distribution is peaked around 0° with a minimum at around 40° the O$^+$ signal increases again peaking at about 90°. Careful examination of the covariance map given in Cornaggia, 1996b, also appears to show this second distribution within the C$^+$-O$^+$ island, shown at position b on Figure 6.8.

The simulated covariance map in Cornaggia, 1996b, was produced by a fit to his data with the critical distance, $\theta$ and $\alpha$ as variables described in Section 1.8. He carried out a Monte Carlo simulation and found the positions of the ions on the covariance map for a variety of bond lengths, alignment angles and bend angles. By comparison of the simulation island peaks and the experimental covariance map the bond length at dissociation and range of orientation and bend angles were determined, and are given in Table 6.9. However, he does not simulate a fit to the distributions produced by ions dissociating at wider angles, shown on Figure 6.8 as position b.
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Table 6.9: Molecular orientation of the CO$_2$ molecule dissociatively ionizing in an intense laser field found by comparing simulated and experimental covariance maps (Cornaggia, 1996b). The notation is described in Section 1.8.

<table>
<thead>
<tr>
<th>Channel</th>
<th>$\Delta \theta_{1/2}$</th>
<th>$\Delta \alpha_{1/2}$</th>
<th>$\Delta R_{1/2} / R_a$ (C-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,1,1)</td>
<td>30</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>(1,2,1)</td>
<td>20</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>(1,2,2)</td>
<td>20</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>(2,2,2)</td>
<td>15</td>
<td>20</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The simulation adequately describes the island at position a, as shown by Figure 6.8. The ion distribution at position b is the part of the island formed by O$^+$ ions from the low energy part of their energy distribution and C$^+$ ions from the high energy part of their energy distribution. This means that the component of momenta of the oxygen ions in the direction of the TOF axis (and laser polarization direction) are small and the carbon ions are large.

A possible explanation for the oxygen ion peak at 0° and at large angles (≈ 90°) is that there are two possible orientations of the molecules in the laser field; the O-O axis parallel and also perpendicular to the laser polarization direction. The mechanism by which diatomic or triatomic molecule re-orients will involve the polarizability and it is using this parameter that a possible explanation for the two molecular orientations can be deduced.

The induced dipole moment perpendicular to the molecular axis is $\mu_{\perp} = \alpha_{\perp} \cos \theta$ and parallel to the molecular axis is $\mu_{\parallel} = \alpha_{\parallel} \sin \theta$ where $\alpha_{\perp}$ and $\alpha_{\parallel}$ are the polarizabilities of the molecule perpendicular and parallel to the molecular axis respectively. The two torques cause the molecule to rotate; one rotates the molecule clockwise field and the other anti-clockwise. The torque on the molecule is the cross product of the induced dipole moment and the electric field and so, depending on the original orientation of the molecule, one torque, $\tau(\perp) = \varepsilon \mu_{\perp} \cos \theta$, will drive the molecule into an orientation perpendicular to the laser field direction and the other torque, $\tau(\parallel) = \varepsilon \mu_{\parallel} \sin \theta$, into an orientation parallel to the laser field direction. The torques can be rewritten as $\tau(\perp) = \alpha_{\perp} \varepsilon^2 \sin \theta \cos \theta$ and $\tau(\parallel) = \alpha_{\parallel} \varepsilon^2 \cos \theta \sin \theta$ which show that it is the relative magnitude of the polarizabilities parallel and perpendicular molecular axis which determine the final molecular orientation. Since, for a linear molecule the polarizability perpendicular to the molecular axis is about half as for the polarizability parallel to the molecular axis.
the molecule will always align parallel to the field. The same can be assumed for a linear triatomic molecule. However, if the molecule bends the ratio of the polarizability parallel and perpendicular to the molecular axis may change. At some bend angle the polarizability of the molecule perpendicular to the field may be greater than the polarizability parallel to it. Thus, due to the range of bend angles produced in the vibrational motion of the molecule it is possible that a percentage will align perpendicular to the laser polarization direction (Seideman, 1998). Figure 6.9 shows the directions of the triatomic molecule with respect to the component of the laser field.

The first distribution, shown at position a on Figure 6.8, will be due to the re-orientation of the molecule parallel to the laser field direction and also accounts for the oxygen ions peaked at 0° on Figure 6.7. This orientation will occur for molecules where the polarizability is greater along the molecular axis than perpendicular to it, (when the O-C-O angles are large), as shown in Figure 6.9(a).

Evidence for the orientation of the molecule perpendicular to the laser field direction is found in the form of the covariance map distribution at position b on Figure 6.8 and corroborated by the oxygen ion distribution peaked at 90°, shown on Figure 6.7. This orientation will occur for molecules where the polarizability is greater perpendicular to the molecular axis than parallel to it, caused by a bend in the molecule, as shown in Figure 6.9b. The range of bend angles which produce the

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure69.png}
\caption{Modification to the ratios of the polarizabilities perpendicular and parallel to the molecular axis for the extremes of the bending vibration of ground state CO$_2$.}
\end{figure}
perpendicular orientation could well be smaller than for parallel alignment, since the amount of ions which have been detected with trajectories matching this orientation are small compared to the number from the parallel orientation, as shown in Figure 6.7. However, an alternative explanation could be that, as postulated in Codling et al, 1987, the probability of ionization perpendicular to the field is less than parallel to it, due to the different distortions of the molecular potentials for the two laser polarization directions.

The final piece of corroborating evidence for the existence of the molecular orientation perpendicular to the laser field direction is that the angular distributions for the carbon ions shown on the polar plots in Figure 6.6 do not decrease to zero at 0°. A proportion of the carbon ions have trajectories parallel to the laser polarization direction. Figure 6.10 shows the two orientations of the molecules parallel and perpendicular to the laser field direction.

![Diagram of CO2 molecules]  

**Figure 6.10:** The two orientations of CO\(_2\) molecules postulated to occur in the femtosecond laser.

Figure 6.7 shows that the amount of oxygen signal at high angles decreases for higher stages of ionization. The second distribution of oxygen ions at larger angles is clearly evident in the (1,1,1) channel and some residual signal remains in the (1,2,1) channel, but none can be observed in the (2,2,2) channel. Table 6.7 shows that the n parameter increases with increasing order of the channel. To put it another way the tightness of the distribution, or alignment with respect to the laser polarization direction, is increasing with increasing order of the channel. With molecules well aligned to the field it seems likely that bent molecules would ionize less producing lower order channels.
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6.3.4 Conclusion of the Angular Detection Results

The majority of the molecules in the laser field are oriented parallel to the laser electric field and the carbon atom has been shown to be perpendicularly displaced creating a bend in the molecule. This has been determined by observing that most of the oxygen ion trajectories are parallel and most of the carbon ion trajectories are perpendicular to the laser field polarization direction. A second, less prevalent, orientation seems to exist where the CO$_2$ axis is perpendicular to the laser field polarization direction and the carbon atom is displaced away from this axis in a perpendicular direction. This has been shown to occur by observing that there is a second ion distribution peaked at 90° for the oxygen ions and that the carbon ion distribution never approaches zero showing that the carbon ions have some kinetic energy for trajectories parallel to the laser field.

6.4 Vibrationally Excited CO$_2$

To date all work on laser fragmentation of molecules has been concerned with molecules initially in the lowest vibrational level but in this section laser experiments have been carried out on molecules which have been excited to upper vibrational levels (nnn). The method used to vibrationally excite the molecules is collisional excitation. The apparatus used for this purpose, Kanthal heating wire wrapped around a hypodermic needle, has been described in Sections 2.2.2 and 2.6.

As has been mentioned previously in Section 6.1 26% of the molecules will be in the excited vibrational states; specifically, assuming the normal Boltzmann distribution, 19% of the CO$_2$ molecules will be in the first excited state which is 83 meV above the vibrational ground state energy. This vibrational state is a bending mode (010) with a minimum bend angle of 156° (Tennyson and Newell, 1998).
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Table 6.10: Operating parameters to obtain TOF spectra of vibrationally excited CO₂ in intense femtosecond laser field.

<table>
<thead>
<tr>
<th>Operating parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser repetition rate</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Laser wavelength</td>
<td>750 nm</td>
</tr>
<tr>
<td>Laser pulse width</td>
<td>60 fs</td>
</tr>
<tr>
<td>Peak laser intensity</td>
<td>$7 \times 10^{15}$ W/cm²</td>
</tr>
<tr>
<td>Keldysh parameter</td>
<td>0.14</td>
</tr>
<tr>
<td>Extraction field range</td>
<td>300 V/cm</td>
</tr>
</tbody>
</table>

6.4.1 An Investigation of the Out-gassing Contaminants from the Heated Kanthal Wire

An investigation was carried out into the background TOF spectra recorded with the Kanthal wire heated. This was necessary to ensure that the differences due to the out-gassing of the Kanthal wire between the TOF spectra recorded with the Kanthal wire heated and unheated could be distinguished from differences due to the dissociation ionization of molecules from vibrationally excited states.

Figure 6.11: TOF spectra in the absence of a test gas (Residual pressure $4 \times 10^{-10}$ mbar) showing the contamination peaks due to the Kanthal wire being heated.
The prominent contamination features, in the spectra shown in Figure 6.11, are $\text{H}_2\text{O}^+$, $\text{OH}^+$, $\text{O}^+$ and $\text{O}^{2+}$ TOF peaks. These features arise from the ionization and dissociative ionization of $\text{H}_2\text{O}$ evaporated from surfaces by the action of the heater. Thus, apart from these contamination peaks any differences between the spectra recorded with ground state and vibrationally excited $\text{CO}_2$ are due to the vibrational excitation of the $\text{CO}_2$ molecules.

The number density of molecules in the gas beam was the same for both 293 K and 473 K which is necessary in order to directly compare the two spectra. Since 
\[
\frac{mv^2}{2} = \left(\frac{3}{2}\right)kT
\]
the number density decreased as $(T)^{3/2}$. However, since the hypodermic was heated, the flow rate out of the needle changed as $\nu$, which is proportional to $(T)^{3/2}$. Consequently the increased flow rate offset a potential reduction in the number density. Thus, a direct comparison of the vertical axis of the TOF spectra taken at 293 and 473 K can be made.

A further consideration in the analysis of the kinetic energies of the ionic fragments is possible broadening of the spectra due to the Doppler effect. The velocity, $V_T$, associated with the thermal motion of the molecules will compound with the velocity, $V_D$, due to the dissociation energy resulting in the total velocity of $V_T + V_D$. The path of the ion along the TOF mass spectrometer will result in a gain of $V$ m/s from the extraction and acceleration fields. Equation 6.3 gives the difference, $\Delta t$, in the time of arrival due to the compounding of the thermal motion of ions with the dissociative velocity.

\[
\Delta t = \left[\frac{2V_T}{(V + V_D)^2 - V_T^2}\right] \approx \frac{2V_T}{(V + V_D)^2}l
\]

Where $l$ is the distance the ions move in the drift region. An extreme case would, for example, be where, $\text{O}^+$ has 1 eV dissociation energy ($V_D = 3.44 \times 10^3$ m/s) and the ion gains 1000 eV from the spectrometer fields (1.09 x 105 m/s). The $\text{CO}_2$ molecule has only thermal energy (4.09 x 102 m/s at 293 K and 5.15 x 102 m/s at 473 K). Using Equation 6.3 $\Delta t$ for 293 K can be calculated to be 8.18 ns and 10.3 ns at 473 K. A comparison of the 293 and 473 K spectra give a time difference of 2.12 ns. Since the bin width of the MCS is 5 ns the effect of increased thermal
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motion due to increased energy is non-resolvable under the present conditions. Therefore, any difference in the two temperature spectra can not be attributed to the Doppler motion of the particles.

6.4.2 TOF Spectra of the Dissociative Ionization of CO$_2$ Molecules, at Room Temperature and 473 K, in a Femtosecond Laser Field

Figure 6.12 shows both the TOF spectra recorded when the CO$_2$ molecules were at room temperature and when they were heated to 473 K. Both spectra were recorded for the same number of laser pulses.

Figure 6.12: TOF spectra of the dissociative ionization of CO$_2$ at room temperature (blue line) and heated to 473 K (red line) recorded when the laser polarization was parallel to the TOF axis. The laser intensity was 7 x 10$^{15}$ W/cm$^2$ and the ambient gas pressure 1 x 10$^{-7}$ mbar.

Several differences between the two spectra shown in Figure 6.12 can be observed. Firstly, the contaminants must be noted such that only the differences due to vibrational excitation of the molecules are analyzed. There is a significant peak of H$_2$O$^+$ and OH$^+$ on the far right of the spectra. Other differences are due to the heating of the molecules. The amounts of O$^+$ and particularly C$^+$ have increased, as shown in Table 6.11, while the number of ions of the higher stages of ionization have decreased except for C$^{2+}$, as shown in Figure 6.11. The increase is due to the increased number of ions in the wings of the peak. Notably the width of the C$^+$ peak more than doubled. It should be noted that the backward O$^{3+}$ peak has
been centred on the C²⁺ feature. However, this overlap does not contribute to the increased width of the C³⁺ feature as the resolved forward O³⁺ peak clearly has the same width for both spectra. For O²⁺ and O³⁺ the overall signal decreased, but less at the wings of the peaks.

Table 6.11: The ratios of counts per pulse under the fragment ion peaks for spectra recorded with CO₂ heated to 473 K and at room temperature.

<table>
<thead>
<tr>
<th>Ions produced by the dissociative ionization of CO₂</th>
<th>Ratio of integrals under the TOF peaks.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Room temp : 473 K</td>
</tr>
<tr>
<td>CO₂⁺</td>
<td>1 : 0.78</td>
</tr>
<tr>
<td>Energetic CO⁺</td>
<td>1 : 2.30</td>
</tr>
<tr>
<td>Thermal CO⁺</td>
<td>1 : 3.43</td>
</tr>
<tr>
<td>CO₂²⁺</td>
<td>1 : 0.77</td>
</tr>
<tr>
<td>Energetic O⁺</td>
<td>1 : 1.85</td>
</tr>
<tr>
<td>Thermal O⁺</td>
<td>1 : 1.41</td>
</tr>
<tr>
<td>C⁺</td>
<td>1 : 2.24</td>
</tr>
<tr>
<td>O⁺²</td>
<td>1 : 0.91</td>
</tr>
<tr>
<td>C⁺²</td>
<td>1 : 1.17</td>
</tr>
</tbody>
</table>

The kinetic energy distributions were found as described in Section 2.5.1. Table 6.12 shows a comparison of the FWHM of the kinetic energy distributions for the ion peaks for both the spectra recorded with the molecules at room temperature and recorded with the molecules at 473 K. The peak kinetic energies have not been shown since they remained the same for both spectra, and are given in Table 6.6.

Figure 6.13 shows the spectra recorded with the laser polarization perpendicular to the TOF axis for molecules heated to 473 K (shown on the figure as the red line) and for molecules at room temperature (shown on the figure as the blue line). The modifications to the spectrum due to heating are remarkably similar to the spectra recorded with the laser polarization parallel to the TOF axis.
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Table 6.12: The FWHM for some of the ions formed in the dissociative ionization of CO$_2$ when the molecules were at room temperature and at 473 K.

<table>
<thead>
<tr>
<th>Ion</th>
<th>FWHM (eV) of ion peaks for spectra recorded with molecules at room temperature</th>
<th>FWHM (eV) of ion peaks for spectra recorded with molecules at 473 K.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$^+$</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>C$^+$</td>
<td>2.0</td>
<td>5.0</td>
</tr>
<tr>
<td>O$^{2+}$</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>C$^{2+}$</td>
<td>3.0</td>
<td>3.5</td>
</tr>
<tr>
<td>O$^{3+}$</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>C$^{3+}$</td>
<td>5.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Figure 6.13: TOF spectra of the dissociative ionization of CO$_2$ at room temperature (blue line) and heated to 473 K (red line) recorded when the laser polarization was perpendicular to the TOF axis. The laser intensity was $7 \times 10^{15}$ W/cm$^2$ and the ambient gas pressure $1 \times 10^{-7}$ mbar.

There are more C$^+$ ions with higher component of momentum along the TOF axis for the spectra recorded with the perpendicular polarization and molecules at 473 K than for the spectra recorded with the same laser polarization but molecules at room temperature. Also the peaks for higher charge states (C$^{2+}$, O$^{2+}$ and C$^{3+}$) are all decreased on the spectra recorded at 473 K. The number of O$^{3+}$ ions detected, however, has increased, due to the increase in the amount of ions in the tail of the C$^{2+}$ ion peak.
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6.4.3 Analysis of the Energy Distributions of the Vibrationally Excited and Ground State Spectra

The energy distributions given in Figure 6.14 and 6.15 were determined from spectra recorded with the laser polarization parallel to the TOF axis. The FWHM of the energy distribution of C⁺ peak given in Figure 6.14, has increased from 2.0 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 O²⁺ TOF peaks at around 30 eV, as shown in Figure 6.13. The relative amounts of C⁺ in the peaks from the two spectra is dramatically different. There is almost double the C⁺ detected in the spectra recorded with the molecules at 473 K compared with the spectra recorded at room temperature. In Figure 6.14 the FWHM of C²⁺ has increased from 3.0 eV to 3.5 eV and a high energy tail is visible up to 30 eV. However, the C³⁺ FWHM remains the same for the spectra recorded at both temperatures.

Figure 6.14: Kinetic energy distribution of C⁺, C²⁺ and C³⁺ fragment ions derived from the peak produced by the forward moving ions in the spectra recorded when the CO₂ molecules were at room temperature (blue line) and at 473 K (red line).
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There appears to be no significant modification to the oxygen ion kinetic energy FWHM. Figure 6.15 shows the oxygen ion kinetic energy distributions from spectra recorded when the CO₂ molecules were heated to 473 K and when they were at room temperature. The distributions were derived from the forward part of the TOF distribution under which there is no OH⁻ contamination from the background gas. The figure shows that there is more O⁺ observed in the spectrum recorded when the CO₂ molecules were heated than in the spectrum recorded when the CO₂ molecules were at room temperature, with slightly more enhancement at low kinetic energies. However, O²⁺ and O³⁺ show a marked decrease in the number of ions recorded with molecules at 473 K. The oxygen ion kinetic energy distributions are shown in Figure 6.15.

Figure 6.15: Kinetic energy distributions of O⁺, O²⁺ and O³⁺ fragment ions, derived from the peak produced by the forward moving ions in the spectra recorded when the CO₂ molecules were at room temperature (blue line) and at 473 K (red line). A contribution due to the C⁺ ion, derived from the forward part of the C⁺ TOF distribution, has been subtracted from the O⁺ high-energy tail with the remaining O⁺ shown as the green line.
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6.4.4 Discussion of Vibrationally Excited CO₂ Results

The differences in the spectra recorded for both laser polarizations for the dissociative ionization of heated and room temperature CO₂ have been summarized in Table 6.13. The orientation and geometry of the molecules for spectra recorded for room temperature molecules have been speculated upon in Section 6.3 and are shown in Figure 6.16 (a) and (c). Figure 6.16 (b) and (d) show the possible orientations for molecules at 473 K in the laser field.

Table 6.13: The differences in the spectra recorded for both laser polarizations for the dissociative ionization of heated and room temperature CO₂.

<table>
<thead>
<tr>
<th>Comparisons between hot and cold CO₂ for parallel polarization:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) C⁺ and C⁴⁺ energy distributions broadened for spectra of heated molecules</td>
</tr>
<tr>
<td>2) O⁺ increased in number especially for low energies for spectra of heated molecules</td>
</tr>
<tr>
<td>3) O⁴⁺ and O⁴⁺ slightly less in number for spectra of heated molecules</td>
</tr>
<tr>
<td>4) C⁵⁺ slightly less in number for spectra of heated molecules</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Comparisons between hot and cold CO₂ for perpendicular polarization:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) C⁺ and C⁴⁺ energy distributions broadened for spectra of heated molecules</td>
</tr>
<tr>
<td>2) O⁺ increased in number especially for high energies for spectra of heated molecules</td>
</tr>
<tr>
<td>3) O⁴⁺ slightly less in number for spectra of heated molecules</td>
</tr>
<tr>
<td>4) C⁵⁺ and C⁵⁺ slightly less in number for spectra of heated molecules</td>
</tr>
</tbody>
</table>

The bigger bend in the molecule due to vibrational excitation could result in more molecules being re-oriented perpendicular to the laser field and it is possible that the bend in the molecule oriented in this way may increase (Seideman, 1998). The decreased bend angle in both orientations can account for the increase in width for the spectra recorded with the molecules at 473 K for both laser polarizations.

This increased bend for both orientations of the molecule in the spectra recorded with heated molecules can also account for more O⁺ in the spectra recorded with laser polarization parallel to the TOF axis. The larger bend may allow more O⁺ ions from the perpendicular orientation to be detected. The O⁺ from this perpendicular orientation will have an apparently lower energy than from the parallel orientation since it will have lower momentum parallel to the TOF axis. The increase in the O⁺ ions at low kinetic energies suggests that more molecules are in this perpendicular orientation and that when they dissociate they are producing more O⁺ than O²⁺ or
O\(^3^+\). The higher charge states O\(^2^+\), O\(^2^+\), O\(^3^+\) and O\(^3^+\) are less numerous for the heated spectra for laser polarizations both parallel and perpendicular to the TOF axis.

\[ \uparrow \varepsilon \uparrow \text{TOF} \quad \text{Room temp (293 K)} \]

(a)

\[ \uparrow \varepsilon \quad \uparrow \text{TOF} \quad \text{Heated (473 K)} \]

(b)

\[ \uparrow \varepsilon \quad \uparrow \text{TOF} \quad \text{Room temp (293 K)} \]

(c)

\[ \uparrow \varepsilon \quad \uparrow \text{TOF} \quad \text{Heated (473 K)} \]

(d)

Figure 6.16: Summary of the summaries for the orientations and bend geometry of the molecule for parallel and perpendicular laser polarization directions with respect to the TOF axis for both heated and room temperature CO\(_2\) gas. The angle \(\delta\) is an unquantified value.

Cornaggia et al, 1996a, also found that for unexcited CO\(_2\) the closer the molecules were aligned with the field the higher the charge states produced. This is probably because for the higher channels good alignment with the field is required to remove the electrons. Thus, for CO\(_2\) it is possible that the bigger bend in the molecule for both orientations leads to less of these higher charge states for both orientations.

The same discussion of the modified polarizabilities holds for the vibrationally excited molecules as for the ground state molecules. The difference is that more of the molecules will be in the perpendicular geometry for the spectra recorded with the heated molecules since 26% of the molecules will be vibrating to a peak angle of 156° whereas the ground state molecules will only be vibrating to a peak angle of 174° prior to the field interacting with the molecules. It has been postulated in this chapter that the bend angle of the molecule increases due to the laser field but the
mechanism by which this occurs is not yet understood.

If the bend angle is increased it is expected that due to the law of conservation of momentum the kinetic energy of the carbon ions will increase. However, when Coulomb explosion takes place the energy which the carbon ion gains is large compared to that of the oxygen ions due to the conservation of momentum. The result is wider carbon ion peaks but no significant change in the widths of the oxygen peaks, as seen in Figures 6.12 and 6.13. Evidence for this process also comes from the observation by Cornaggia et al, 1996a, in an experiment using \( \text{SO}_2 \), which is a bent molecule. The \( \text{O}^+ + \text{S}^+ + \text{O}^{2+} \) channel (where \( Z = 1 \) or \( 2 \)) was shown to exhibit an almost elliptical island, or more precisely an atoll on a covariance map produced with laser polarization parallel to the detector axis, as shown in Figure 6.17.

![Figure 6.17: Segment of the Covariance map of SO\(_2\) showing the usual atoll shape of the correlation island of S\(^-\)-O\(^+\) (Cornaggia et al, 1996a).](image)

The ellipticity was shown to be due to the bend in the molecule, and is consistent with \( \gamma = 120^\circ \), which was the known molecular bend. The fact that the atoll was almost complete is not commented on in their paper but indicates that the alignment angle \( \theta \) ranges between 0\(^\circ\) and 90\(^\circ\) although the signal at 90\(^\circ\) was between 2 and 5 times less intense than at 0\(^\circ\). In the present work it was assumed that the equilibrium C-O bond length of 1.16 Å was constant. For molecules in the perpendicular orientation the bend angle can be varied and the Coulomb energies for the C\(^+\) ions from the \( \text{O}^+ + \text{C}^+ + \text{O}^+ \) channel have been calculated. For \( \gamma = 90^\circ \) it is possible to generate an energy of 13.7 eV, which is in the tail of the measured C\(^+\) energy distribution given in Figure 6.14. This reaction produces O\(^+\) ions which have only 2.6 eV of kinetic energy.
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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. For the perpendicular orientation, with $\gamma$ set to $90^\circ$, the $C^2+$ energy, for ions from the $O^2+ + C^2+ + O^2+$ channel, has been calculated to be 55 eV, which is higher than that observed. This is consistent with the probability that higher stages of ionization result mostly from molecules oriented parallel to the laser polarization direction.

6.4.5 Conclusion

This chapter has described the investigation of laser induced dissociative ionization of CO$_2$ both in its ground state and vibrationally excited states, with observation of the excited CO$_2$ fragmentation obtained for the first time. The results obtained with CO$_2$ in the ground state show that a small population of lower charge states are produced from alignment perpendicular to the field, but that for CO$_2$ in excited states a larger population of lower charge states is produced in this alignment. In both cases alignment parallel to the laser field is dominant. In all cases discussed the molecule is bent. Bending appears to be increased by the field when the molecule is in a vibrational bend mode.
Chapter 7: Femtosecond Laser Pulse
Dissociative Ionization of Sulphur Hexafluoride

7.0 Introduction

This chapter contains a report of the interaction of femtosecond laser pulses with SF$_6$. This is the first work in which the fragmentation pattern of SF$_6$ has been discussed in any detail when subjected to the influence of intense laser electric fields.

Sulphur Hexafluoride is formed by a central sulphur atom surrounded by a cage of electronegative fluorine atoms, and has octahedral geometry, as shown in Figure 7.1. The bond length of all of the S-F bonds is 1.58 Å (Sutton et al., 1958). It has a zero permanent dipole moment in its ground state.

\[ r_1 = 1.58 \text{ Å} \]

Figure 7.1: The octahedral geometry of the SF$_6$ molecule
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Table 7.1: The operating conditions for the data collected during the experiments of SF₆ with femtosecond laser pulses.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser repetition rate</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Laser wavelength</td>
<td>750 nm</td>
</tr>
<tr>
<td>Laser pulse width</td>
<td>60 fs</td>
</tr>
<tr>
<td>Laser intensity range</td>
<td>$4 \times 10^{14}$ to $8 \times 10^{15}$ W cm⁻¹</td>
</tr>
<tr>
<td>Extraction field range</td>
<td>10 - 600 V/cm</td>
</tr>
</tbody>
</table>

7.1 Designation of the Ion Peaks on Spectra of the Dissociative Ionization of SF₆

Figure 7.2 shows the fragmentation TOF spectrum for SF₆ recorded with an applied extraction field of 300 V/cm, when the laser polarization direction is parallel to the TOF axis.

![TOF spectrum](image)

**Figure 7.2**: TOF spectrum of the dissociative ionization of SF₆ recorded with an extraction field of 300 V/cm, when the laser polarization direction is parallel to the TOF axis. The laser intensity was $7 \times 10^{15}$ W/cm² and the ambient gas pressure was $1 \times 10^{9}$ mbar.

The first feature of note is that no SF₆⁺ ions are observed, the most massive fragment ion being SF₅⁺. This is the only feature of the ion mass spectrum that has previously been commented upon in relation to short pulse laser induced
dissociative ionization. (Lynga et al, 1996). This observation is in fact to be expected as the parent ion is known to dissociate, over a period of around one picosecond, into a range of fragment ions (Creasy et al, 1991 and 1993). That part of the fragmentation pattern which extends from \( S^+ \) to \( SF_5^+ \), in Figure 7.2, is typical of the distribution of ions formed by both electron impact ionization, shown in Figure 7.3, and synchrotron photo ionization (Hitchcock and Van der Weil, 1978 and Hitchcock et al, 1979) and is the signature of \( SF_5^+ \) production.

In general the parent ion is usually prominent in experiments using femtosecond pulses. Although it has been shown that femtosecond pulses can overcome the propensity of certain molecules to pre-dissociate during intense laser field ionization (Ledingham et al, 1995) it is impossible in the case of \( SF_6 \) as the dissociation occurs post ionization due to the ground state of \( SF_6^+ \) being a repulsive state.

The appearance of doubly charged fragment ions \( SF_4^{2+} \) and \( SF_2^{2+} \) indicates that the parent ion has been doubly charged since there is no interaction between the laser pulse and any of the dissociated fragment ions because dissociation takes much longer (1 ps) than the duration of the laser pulse (60 fs). The formation of \( SF_6^{2+} \) also leads to Double Dissociative Ionization (DDI) in which \( SF_6^{2+} \) dissociates into two fragment ions \( SF_5^+ \) and \( F^+ \) (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).
Figure 7.4: TOF spectra of the fragmentation of $SF_6$ in a 60 fs laser field with the laser polarization parallel to the TOF axis, and recorded with extraction fields of (a) 300, (b) 150 and (c) 75 V/cm.

The TOF peaks of energetic and thermal ions for different species significantly overlap for all of the extraction fields used and so in order to designate these peaks...
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the extraction field was gradually altered from 10 to 600 V/cm, and the resulting TOF spectra observed. As the extraction field was 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. Figure 7.4 shows the TOF spectra recorded with extraction fields of (a) 300, (b) 150 and (c) 75 V/cm.

Several notable differences can be seen between the three spectra shown in Figure 7.4. Firstly, the TOF peak due to the forward moving F⁺ ion passes across the S⁵⁺ ion peak from right to left with decreasing extraction field. Secondly, the peaks due to the forward and backward moving F²⁺ ion are superimposed on the S⁺⁺ and S³⁺ ion peaks respectively in the spectrum recorded with a 300 V/cm extraction field. However, as the extraction field decreases the peak due to the forward moving F⁺⁺ ions moves away from the S⁺⁺ ion peak to the left and the peak due to the backward moving F⁺⁺ ions moves away from the S³⁺ ion peak to the right. Thirdly, the peak due to the backward moving F³⁺ ions passes across the S⁺⁺ ion peak from right to left with decreasing extraction field. This evidence suggests that the peaks have been correctly designated since they are behaving as expected for the changing extraction fields.

7.2 Analysis of the SF₆ TOF Spectra

Any overlap of the high kinetic energy ion peaks and thermal ion peaks, in the case of a diatomic molecule, can be easily investigated by rotating the direction of the laser polarization 90° (Normand et al, 1992a, and 1992b), as discussed in Section 2.5.1, since it is known that the energetic fragments produced in the MEDI process are strongly aligned with the laser field (Hatherly et al, 1990). Due to the geometry of the SF₆ molecule, shown in Figure 7.1, this type of analysis is not as complete. The bond angles in SF₆ are 90° in the ground state, which is a spherically symmetric molecular geometry. Thus, both laser polarization directions result in the possibility of a F-S-F axis being parallel with the TOF axis. However, when the laser polarization direction is perpendicular to the TOF axis the two F-S-F axes
perpendicular to the laser polarization direction (skirt ions) are randomly oriented with respect to the TOF axis, as shown in Figure 7.5 (a).

**Figure 7.5:** The alignment of the SF₆ molecule with respect to the laser polarization direction and the TOF axis, assuming that there is no modification to the molecular geometry by the laser field. The laser polarization is (a) perpendicular and (b) parallel to the TOF axis.

Assuming that there is good alignment of one of the F-S-F axes of the molecule with the laser field, that there is no distortion of the octahedral symmetry of the molecule and that the F-S-F atoms dissociatively ionize into symmetric channels when subjected to the laser field, the spectrum recorded with the laser polarization parallel to the TOF axis might be expected to show one zero energy peak, from the skirt fluorine ions, as well as forward and backward energetic peaks from the fluorine ions along the TOF axis. However, when the laser polarization direction is perpendicular to the TOF axis it might be expected that these peaks will be broadened to lower kinetic energies positions in the TOF spectrum and perhaps merged due to the non-alignment of the two skirt F-S-F axes with the TOF axis, as shown in Figure 7.5(a). These scenarios would only occur if the angular acceptance of the TOF system for the specified ions were 180°.

The width of the fluorine ion peaks in the spectrum recorded with the laser polarization direction perpendicular to the TOF axis will depend heavily on the angular acceptance of the detector. If the angular acceptance is less than 180° then the ions from Coulomb explosions moving perpendicular to the TOF axis will remain undetected such that no zero energy peak appears on the TOF spectrum.
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Figure 7.6: The angular acceptance, $\theta$, of the forward moving $F^+$, $F^{2+}$ and $F^{3+}$ ions for a 300 V/cm extraction field.

If the angular acceptance of the detector is greater than the range of alignment angles of the F-S-F axis, but less than 180°, for the spectrum recorded with the laser polarization direction parallel to the TOF axis, then the $F^+$ ion peaks on the spectrum recorded with the laser polarization direction perpendicular to the TOF axis will be wider due to the random alignment of the two F-S-F axes with respect to the TOF axis.

Figure 7.7: TOF spectra of the dissociative ionization of SF$_6$ in a 60 femtosecond laser field recorded with a 300 V/cm extraction field. The laser intensity is $7 \times 10^{15}$ W/cm$^2$ and the ambient gas pressure 2 x $10^8$ mbar. Spectra for both laser polarizations (parallel and perpendicular to the TOF axis) are shown.
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Figure 7.6 gives the angular acceptances for the F⁺, F²⁺ and F³⁺ for an extraction field of 300 V/cm. The angular acceptance of the forward moving F²⁺ (50 eV) ions is 30° and is 37° for the forward moving F⁺ (17eV) ions. The F⁺ and F²⁺ peaks are wider in the spectra recorded with laser polarization perpendicular to the TOF axis than in the spectra recorded with laser polarization parallel to the TOF axis, as shown in Figure 7.7. This indicates that the range of alignment angles for the well-aligned F-S-F axis involving the F²⁺ (50eV) ion is less than 30°. A similar argument for the F⁺ (17 eV) ions can be put forward, such that the range of alignment angles of the well-aligned axis involving the F⁺ (17 eV) ion is less than 37°.

![Figure 7.8: The angular acceptance, θ, of the forward moving F⁺, F²⁺ and F³⁺ ions for a 75 V/cm extraction field.](image)

Figure 7.9 shows the TOF spectra of the dissociative ionization of SF₆ recorded with an extraction field of 75 V/cm. The TOF peaks due to the forward and backward moving energetic F²⁺ ions are distinct from the S³⁺ and S⁴⁺ ions which is not the case for the spectrum recorded with a 300 V/cm extraction field.

The ratio of the energetic fluorine ions relative to the low energy ions S²⁺ to SF₅⁺, has decreased considerably compared to the spectrum recorded with a 300 V/cm extraction field, due to a reduction in the angular acceptance of the detector for the lower extraction field, as shown in Figure 7.8. The low energy ion peaks from S²⁺ to SF₅⁺ show the same sizes relative to each other for both laser polarization directions. This is expected as the angular acceptance of the TOF spectrometer is 180° for these ions.

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Figure 7.9: TOF spectra of the dissociative ionization of SF₆ recorded with a 75 V/cm extraction field when the laser polarization direction was parallel and perpendicular to the TOF axis. The laser intensity was 7 x 10¹⁵ W/cm² and the ambient gas pressure was 2 x 10⁻⁸ mbar.

7.2.1 Determination of the Appearance Intensities of Ions Produced in the Dissociative Ionization of SF₆

Spectra were recorded with an extraction field of 300 V/cm for a range of different laser intensities (7 x 10¹⁵, 4 x 10¹⁵, 1.8 x 10¹⁵, 8 x 10¹⁴ and 4.3 x 10¹⁴ W/cm²). The intensities were determined from the pulse energy as described in Section 4.2.1 and the intensity was varied as described in Section 3.3.6. The approximate appearance intensities, determined as described in Section 4.2.2, for the various ions are given in Table 7.2.

The values for the appearance intensities are approximate and, due to the intensity increments between the spectra, have intrinsically large errors associated with
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them. The uncertainties shown in the Table 7.4 are simply the intensity increments between spectra recorded at the next lower and higher intensities.

Table 7.2: The appearance intensities for the ionic fragments produced in the dissociative ionization of SF₆ using femtosecond laser pulses.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Appearance intensity (W/cm²)</th>
<th>Uncertainty in the Appearance intensity, ( I_{\text{app}} ) (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F⁺, S⁺ and S²⁺</td>
<td>(&lt; 4.3 \times 10^{14})</td>
<td>(\pm 3.7 \times 10^{14})</td>
</tr>
<tr>
<td>F²⁺, S³⁺ and S⁴⁺</td>
<td>(8 \times 10^{14})</td>
<td>(\pm 6.8 \times 10^{14})</td>
</tr>
<tr>
<td>F⁵⁺ and S⁵⁺</td>
<td>(1.8 \times 10^{15})</td>
<td>(\pm 1.6 \times 10^{15})</td>
</tr>
</tbody>
</table>

7.2.2 Kinetic Energy Analysis of the Ionic Fragments Produced in the Dissociative Ionization of SF₆

The kinetic energies of the fragment ions were determined as discussed previously in Section 2.5. Table 7.3 shows the initial kinetic energies of the fragments from the dissociative ionization of SF₆ using femtosecond laser pulses. The FWHM of the sulphur ions, given in Table 7.3, illustrate that there is possibly some distortion of the molecular geometry in the laser field. The skirt of fluorine ions are pulled out of the plane perpendicular to the laser polarization direction and as this happens the centre of mass moves away from the sulphur ion, as shown in Figure 7.10. Thus, upon dissociation the sulphur ions have a broader kinetic energy distribution than they would have if the molecule were rigid in the field. The FWHM of the kinetic energy distribution broadens for higher stages of ionization. There are three possible explanations.

Firstly, that a greater degree of distortion of the molecule could produce bigger FWHM of the energy distributions, and secondly, that the higher charged ions receive more kinetic energy in the Coulomb explosion process within the same altered geometry as the lower stages of ionization. The third possible explanation as to why the sulphur ion peaks have large FWHM, which does not involve the distortion of the molecular geometry, is that asymmetric fragmentation is taking place, which would result in the sulphur dissociating with some kinetic energy.
Table 7.2: The appearance intensities for the ionic fragments produced in the dissociative ionization of SF$_6$ using femtosecond laser pulses.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Appearance Intensity (W/cm$^2$)</th>
<th>Uncertainty in the Appearance Intensity, $I_{app}$ (W/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F^+$, $S^+$ and $S^{2+}$</td>
<td>$&lt; 4.3 \times 10^{14}$</td>
<td>$\pm 3.7 \times 10^{14}$</td>
</tr>
<tr>
<td>$F^{2+}$, $S^{3+}$ and $S^{4+}$</td>
<td>$8 \times 10^{14}$</td>
<td>$\pm 6.8 \times 10^{14}$</td>
</tr>
<tr>
<td>$F^{4+}$ and $S^{5+}$</td>
<td>$1.8 \times 10^{15}$</td>
<td>$\pm 1.6 \times 10^{15}$</td>
</tr>
</tbody>
</table>

**7.2.2 Kinetic Energy Analysis of the Ionic Fragments Produced in the Dissociative ionization of SF$_6$**

The kinetic energies of the fragment ions were determined as discussed previously in Section 2.5. Table 7.3 shows the initial kinetic energies of the fragments from the dissociative ionization of SF$_6$ using femtosecond laser pulses. The FWHM of the sulphur ions, given in Table 7.3, illustrate that there is possibly some distortion of the molecular geometry in the laser field. The skirt of fluorine ions are pulled out of the plane perpendicular to the laser polarization direction and as this happens the centre of mass moves away from the sulphur ion, as shown in Figure 7.10. Thus, upon dissociation the sulphur ions have a broader kinetic energy distribution than they would have if the molecule were rigid in the field. The FWHM of the kinetic energy distribution broadens for higher stages of ionization. There are two possible explanations.

Firstly, that a greater degree of distortion of the molecule could produce bigger FWHM of the energy distributions, and secondly, that the higher charged ions receive more kinetic energy in the Coulomb explosion process within the same altered geometry as the lower stages of ionization. Another possible explanation as to why the sulphur ion peaks have large FWHM, which does not involve the distortion of the molecular geometry, is that asymmetric fragmentation is taking place, which would result in the sulphur dissociating with some kinetic energy.
Table 7.3: The peak kinetic energies and FWHM of the kinetic energy distributions found from the 1D-TOF spectrum of the dissociative ionization of SF$_6$ using femtosecond laser pulses.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Peak kinetic energy (eV)</th>
<th>FWHM of kinetic energy distribution (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$^+$</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>S$^{2+}$</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td>S$^{3+}$</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>S$^{4+}$</td>
<td>0</td>
<td>1.2</td>
</tr>
<tr>
<td>S$^{5+}$</td>
<td>0</td>
<td>3.0</td>
</tr>
<tr>
<td>F$^+$</td>
<td>2 and 17</td>
<td>---</td>
</tr>
<tr>
<td>F$^{2+}$</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>F$^{3+}$</td>
<td>90</td>
<td>60</td>
</tr>
</tbody>
</table>

${\times}$ instantaneous centre of mass

$\downarrow$ direction of initial motion of the sulphur ion

$Laser polarisation direction$

Figure 7.10: Possible modification to the geometry of the SF$_6$ molecule exposed to a femtosecond laser field.

The fact that all of the sulphur peaks are centred about 0 eV indicates that symmetric channels of MEDI, discussed in Section 1.2, are dominant. In the case of SF$_6$, symmetric channels imply that the two fluorine atoms on each axis have the same stage of ionization. A convenient simplification in the analysis of SF$_6$, then, is to treat each axis as a triatomic molecule sharing the same sulphur atom which gives the three channels F$^{\text{Me}}$ - S$^{\text{Ne}}$ - F$^{\text{Me}}$, F$^{\text{Li}}$ - S$^{\text{Na}}$ - F$^{\text{Li}}$ and F$^{\text{P+}}$ - S$^{\text{Na+}}$ - F$^{\text{P+}}$ in total for one molecule. Figure 7.11 shows the kinetic energy distributions of the fluorine ions found from the spectra recorded with an extraction field of 75 V/cm.
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Figure 7.11: Kinetic energy distributions for $F^+$, $F^{2+}$ and $F^{3+}$ found from the spectra recorded with a 75 V/cm extraction field. The arrows refer to calculated kinetic energies released for MEDI channels given in Table 7.6.

The $F^+$ ions result from both DDI (Hitchcock et al, 1978) and MEDI and two distributions are evident in the $F^+$ energy distribution; a low energy peak at around 2 eV and a high energy shoulder appearing at around 17 eV, which tails off at 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), discussed in Section 1.4. The shoulder at 17 eV represents the peak of the distribution due to MEDI. The $F^{2+}$ distribution has a FWHM of 25 eV and a maximum at around 50 eV while the $F^{3+}$ 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.

A Quattro Pro spreadsheet was designed to calculate the kinetic energy releases of the fluorine ions taking into account the forces due to all the ions (see Appendix 5). Only symmetric processes were considered since the sulphur ions have a peak kinetic energy of 0 eV showing these processes are dominant. The calculation assumes that the SF$_6$ molecule singly ionizes and expands such that the bond lengths reach the critical distance (see references in Section 1.7). At this distance further ionization takes place within a very short space of time (Posthumus et al, 1995b). Table 7.5 shows the results of these calculations.
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7.2.3 MEDI Channel Determination

It is known that kinetic energies resulting from MEDI exhibit a strong relationship with the energies that would be expected from Coulomb explosion from the equilibrium separation of the atoms. Typically the kinetic energies observed are consistent with Coulomb explosions occurring at a single critical internuclear separation for all channels, \( R_c = C_m \cdot R_e \), where \( C_m \) is a constant and \( R_e \) is the equilibrium separation. Table 1.2 gives the calculated and experimental \( R_c \) for several diatomic molecules given in Seideman et al., 1995a. The constant \( C_m \) has been found to be 0.45 for molecules consisting of light molecules such as CO, O\(_2\) and N\(_2\) (Posthumus et al., 1995).

Using the known properties of MEDI the fragmentation symmetry and the 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 some of the allowed MEDI channels can be predicted. 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 (Figures 7.7 and 7.9).

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\(^{2+}\). It is possible to determine the most likely correlations by considering the ionization potentials of the observed fragments since field ionization is a barrier suppression process. Table 7.4 gives the zero field ionization potentials for the sulphur atom and the fluorine atom. Firstly, it should be noted that because the fluorine ionization potentials are further apart than the sulphur ionization potentials 2 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.
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Table 7.4: Zero field ionization potentials of fluorine and sulphur

<table>
<thead>
<tr>
<th>Sulphur ion</th>
<th>Ionization potential (eV)</th>
<th>Fluorine ion</th>
<th>Ionization potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S⁺</td>
<td>10.36</td>
<td>F⁺</td>
<td>17.42</td>
</tr>
<tr>
<td>S²⁺</td>
<td>23.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S³⁺</td>
<td>34.83</td>
<td>F²⁺</td>
<td>34.97</td>
</tr>
<tr>
<td>S⁴⁺</td>
<td>47.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S⁵⁺</td>
<td>72.68</td>
<td>F⁵⁺</td>
<td>62.7</td>
</tr>
</tbody>
</table>

Channels (1) and (2), given in Table 7.5, are the simplest symmetrical channels of MEDI to occur with the production of F⁺. The kinetic energies predicted for channels (1) and (2) are indicated in Figure 7.11 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, at 17 eV, has been assumed to be approximately the peak of the MEDI kinetic energy distribution.

Table 7.5: Calculated Coulomb energies for possible Coulomb explosion fragmentation channels of SF₆ from Rₑ = 3.51 Å. The channel number refers to the energy positions shown in Figure 7.11.

<table>
<thead>
<tr>
<th>Channel</th>
<th>F⁺ energy release (eV)</th>
<th>F²⁺ energy release (eV)</th>
<th>F⁴⁺ energy release (eV)</th>
<th>Total energy release (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SF₆⁷⁺ → S⁺ + 6F⁺</td>
<td>-</td>
<td>-</td>
<td>66</td>
</tr>
<tr>
<td>2</td>
<td>SF₆⁶⁺ → S²⁺ + 6F⁺</td>
<td>15.1</td>
<td>-</td>
<td>90.6</td>
</tr>
<tr>
<td>3</td>
<td>SF₆¹⁴⁻ → S²⁻ + 6F₂⁺</td>
<td>-</td>
<td>43.8</td>
<td>262.8</td>
</tr>
<tr>
<td>4</td>
<td>SF₆¹⁵⁻ → S³⁻ + 6F₂⁺</td>
<td>-</td>
<td>52</td>
<td>312</td>
</tr>
<tr>
<td>5</td>
<td>SF₆¹⁶⁻ → S⁴⁻ + 6F₂⁺</td>
<td>-</td>
<td>60.2</td>
<td>361.2</td>
</tr>
<tr>
<td>6</td>
<td>SF₆¹⁷⁻ → S⁺⁻⁴ + 4F²⁺ + 2F³⁺</td>
<td>-</td>
<td>54.1</td>
<td>88.6</td>
</tr>
<tr>
<td>7</td>
<td>SF₆¹⁸⁻ → S⁴⁻ + 4F²⁺ + 2F³⁺</td>
<td>-</td>
<td>62.3</td>
<td>101</td>
</tr>
<tr>
<td>8</td>
<td>SF₆¹⁹⁻ → S⁵⁻ + 4F²⁺ + 2F³⁺</td>
<td>-</td>
<td>70.5</td>
<td>113.3</td>
</tr>
</tbody>
</table>

It is possible that S⁴⁺ could also be produced in a dissociation channel with F²⁺; however, the ionization potential of S³⁺ is very close to that of F²⁺ making it much more likely that these two ions are produced together. In addition it can be deduced from Table 7.5 that F²⁺ may be formed in dissociation channels with S²⁺ and S³⁺ which is expected to depend on the peak laser intensity. Channels (3), (4) and (5) in
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Table 7.5 are the simplest symmetrical MEDI channels involving F\(^{2+}\). As with F\(^+\) the kinetic energies calculated for F\(^{2+}\) as a result of channels (3), (4) and (5) are in good agreement with the peak of the measured energy distribution.

7.3 Discussion

In accounting for the kinetic energy of the F\(^{3+}\) fragment ion it is necessary to address the question of alignment of the molecule. In the case of F\(^+\) and F\(^{2+}\) the signal recorded with polarization parallel and perpendicular to the spectrometer axis are very similar, as shown in Figure 7.12, and the ratios of 1:1 and 3:2, respectively, can be deduced. For F\(^{3+}\) the anisotropy is much more pronounced having a ratio of a signal parallel to perpendicular of 4:1.

![Figure 7.12: Region of the TOF spectrum recorded with a 300 V/cm extraction field showing the relative heights of the F\(^+\), F\(^{2+}\) and F\(^{3+}\) ions.](image)

The anisotropy of the F\(^{3+}\) ions can be explained by using the barrier suppression mechanism and taking into account the highly symmetric nature of SF\(_6\). If distributed with random alignment the SF\(_6\) molecule always has one axis which makes an angle with the field of less than 45\(^0\) and at the same time the molecule has two partially unaligned axes; they make an angle of more than 45\(^0\) 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 an axis which is unaligned. This will make ionization more likely for the fluorine atoms along the...
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aligned F-S-F axis. The calculations for I₂, Dietrich et al, 1993, estimate that in their experiment this distortion is equivalent in the reduction of 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 unaligned molecules can be compensated for by an increase in the field strength, and hence laser intensity, by a factor of 2.

Alignment is not crucial in achieving a given stage of ionization provided that the laser field strength and hence intensity is high enough. This may well be true in the present experiment where F⁺ and F²⁺ are concerned because the peak laser intensity 7 x 10¹⁵ W/cm² is at least a factor of 8 times higher than the estimated intensity at which these ions appear (8 x 10¹⁴ W/cm²), as shown in Table 7.2. However, it is not true for the production of F³⁺ where the laser intensity is only just above the appearance intensity. Even a 15% reduction in the ionization potential of F³⁺ due to stark shift for those fluorine atoms whose internuclear axis is aligned with the field will be crucial in promoting production of F³⁺. This argument does not require any alignment of the SF₆ molecule by the field.

In Chapter 6 it was shown that higher charge states are produced when the molecular axis is well aligned with the laser field. Most of the F³⁺ ions produced when the laser polarization is perpendicular to the TOF axis will be lost due to the acceptance angles for F³⁺ being <180° for these energies (25 to 150 eV). When the TOF axis and the F-S-F axis producing most F³⁺ are parallel most of the F³⁺ ions should be detected.

The simplest MEDI channels which take into account the observed F³⁺ anisotropy are given in Table 7.5 as (6), (7) and (8) and are indicated by arrows in Figure 7.11. The kinetic energy calculations predict the peak of the energy distribution reasonably well but the distribution is wide for F³⁺ and this aspect cannot be reproduced. The broadened distribution could be attributed to aspects of the MEDI of SF₆ in the femtosecond laser field which have not been taken into account in this work. The distortion of the symmetric structure will have an effect on the kinetic energy distribution of the fluorine ions as well as the sulphur ions and another complication is that it is expected that at least some asymmetric channels will be produced. However, no asymmetric channels have been found for either CO₂ or N₂O dissociatively ionizing in this laser field from the results presented in this thesis. As has been shown in this chapter SF₆ can be modeled relatively successfully as a triatomic.
7.4 Summary

The results and analysis in this chapter have allowed the prediction of some of the fragmentation channels produced in the dissociative ionization of SF$_6$ using 60 fs laser pulses. The alignment and geometric distortion of the molecule have been discussed and the initial kinetic energies of the fragment ions have been determined.
Chapter 8: Suggestions for Future Work

Future investigation

The dissociative ionization channels for diatomic and triatomic molecules are becoming better known. What is less well understood is the geometric modification to molecules by the intense laser field and the mechanisms by which this occurs. What is required is a wider study of the angular distributions of the fragment ions from the dissociating molecules. The expansion of the molecule to the critical distance has been widely investigated. However, bending of the triatomic and larger polyatomic molecules is hardly understood at all. The question is how does the molecule bend? Is the mechanism due to the induced dipole moment, or to the natural polarizability of the molecule, for example?

Further investigation of the geometric modification would involve the development of the technique of collecting TOF spectra for different polarization angles. Instead of producing polar plots, as shown in Figure 6.6, of the number of ions per laser pulse on the radial axis, perhaps a more useful strategy would be to plot the momenta of the ions on the radial axis with a colour scale to indicate the number of counts produced at that momentum value. This is advantageous since it provides more information about the laser-molecule interaction. The direction and energy of the ions can be easily computed. Plotting momentum is more correct for triatomic molecules than plotting kinetic energy, since in these situations, there is often a large component of momentum perpendicular to the TOF axis and so calculating the kinetic energy as shown in Section 2.5 is invalid.

The symmetric nature of CO$_2$ means there is less information to be gleaned from 1D-TOF than for an asymmetric molecule. Nitrous oxide, N$_2$O, was an interesting molecule to study since the non-symmetry produces more energetic ions groups
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than a symmetric molecule. However, the two nitrogen ions complicated the data when it came to speculating on the orientation of the molecule in the laser field. For example, did a nitrogen ion have very low momenta parallel and higher momenta perpendicular to the field or was it a thermal ion? The complexity of the energy groups, especially for the singly charged ions did not make this an easy question to answer, even when the polarization of the molecule was changed perpendicularly. The question could be answered with the use of momenta imaging described above. However, a clearer answer about the directionality of the fragment ions could be better achieved by studying a triatomic molecule with non-symmetry where all three ions were of different species whose masses were not fractions of each other.

Another question which has arisen during the course of the analysis of N$_2$O and CO$_2$ is that the refined field ionization Coulomb explosion model does not appear to supply all the answers for triatomic molecules such as N$_2$O and CO$_2$. It has been found that the Coulomb explosion for both molecules occurs at increasingly high internuclear separations for higher dissociative ionization channels. However, the opposite is predicted for diatomic molecules by this model. The model has been adapted for triatomic molecules by another research worker in our laboratory and it has been found that the model does appear to show the same behaviour for triatomic molecules as it does for diatomic molecules. It is possible that this is due to the fact that the model does not take into account a bend in the molecule and also assumes that the molecule is always well aligned with the field. Several researchers have found that the molecules which are better aligned with the laser polarization direction dissociate into higher order dissociative ionization channels. Further study of other molecules, especially bent molecules such as H$_2$O and SO$_2$, may well enlighten us as to the reason.

The behaviour of polyatomic molecules is even less understood than triatomic molecules. Investigations of hydrocarbon chains have been carried out by Cornaggia et al, 1995, and hydrocarbon molecules by Vijayalakshmi et al, 1997. These publications raised many questions which have not yet been answered specifically about the geometric modification to the field. Vijayalakshmi et al, suggested that they were able to predict the dissociation of the molecules studied by investigation of the modification of the electron density of the molecule by a static electric field. The field of intense laser field interactions with clusters of rare gas atoms is expanding (for example Lesius et al, 1997, Ditmire et al, 1997 and
Shao *et al.*, 1996). However, much scope is left for the investigation of the behaviour of these macro-molecules in the laser field.

The simulation of the covariance map of CO$_2$ by Cornaggia, 1996b, was a very useful technique to help understand the geometry of the molecule prior to Coulomb explosion. In this paper Cornaggia maintained the critical distance and modeled the bend angles of the molecule. Investigations in Chapter 5 (N$_2$O) and Chapter 6 (CO$_2$) have shown that the critical distance is not the same for all channels. This type of simulation could be modified to include this difference in $R_c$ for the different channels. It is important that the alignment, bond lengths and bend angles are all simulated, since they all will contribute to the final motion of the ionic fragment ions.

**Experimental modification**

The ratios of the TOF peaks on the spectrum are dependent on the angular acceptance of the ion. A truer TOF spectrum could be achieved by calculating the angular acceptances for a range of kinetic energies and modifying the number of counts in the spectrum time-bin such that the number of counts featured in the spectrum are what would be detected if the angular acceptance for the ions were all 180°.

One of the most important experimental modifications required is that the data acquisition system is changed from a digital input system (MGS) to an analogue system (Oscilloscope). This has been implemented in the laboratory now and has shown an improvement in the symmetry of the TOF peaks. However, at this point the resolution of the peaks is less than for the peaks on the TOF spectra collected using the MCS. Development of this new input system such that the resolution is better should be implemented in the future.

*In this exciting and expanding field of physics a large number of investigations have already been carried out to try to understand the dynamics of intense laser interactions with atoms and molecules, as shown, in part, in Chapter 1. Although this is the case there is still a huge amount that is not known and has yet to be discovered and excitement lies not just in the development of further understanding of the physics but in the determining of what is as yet unknown.*
Appendix 1:

Determination of the potentials to be applied to the top and bottom plate of the extraction region and the acceleration plate.

The program written to simulate the motion of the ions in the TOF mass spectrometer is given in Appendix 3. The TOF mass spectrometer discussed in this appendix is shown in Figure 2.11. The TOF of ions formed at all positions across the source region were calculated in the course of the program. A graph of these flight times was plotted against the ion formation position during the simulation. From this graph it was possible to determine if the chosen set of potentials would produce a good spacial focus or not. A good focus is produced when the majority of the source region is focused with the same or similar flight time. Figure 1 (a) shows a good and (b) a bad spacial focus.

Figure A1 (a) A good and (b) a bad spatial focus for $N^+$ in the TOF mass spectrometer described in Section 2.5 where $S_J/2$ is the geometric midpoint (0 eV equipotential) in the extraction region and E is the initial kinetic energy of the ion.
Appendix 2:

Derivation of the equation used to find the kinetic energy of the dissociating ions focused by the TOF mass spectrometer

The initial kinetic energy of ions dissociating along the laser electric field and parallel to the time of flight axis, as shown in Figure A2(a), can be calculated from a formula derived from Newton's equations.

![Diagram](image)

Figure A2: (a) Ions dissociating in the extraction region when the laser polarization axis is parallel to the time of flight axis and (b) a section of the resulting TOF spectrum.

In Figure A2 (b) the peak at the earlier flight time results from the ion X in Figure A2(a) and the peak at the later arrival time results from the ion Y in Figure A2(a). The time of flight for each ion can be calculated using SI units in the following way.

The flight time of ion X:

\[ F = ma \quad \text{and} \quad F = Eq \quad a = \frac{Eq}{m} \quad \text{Equation 1} \]

where \( F \) is the force exerted on the particle by the applied electric field, \( E \) is the electric field strength, \( q \) is the charge on the ion and \( m \) is the ion's mass.

The ions initial velocity can be found from its initial kinetic energy value:
where $K_e$ is the initial kinetic energy of the ion and $u$ is the ion's initial velocity. Equation 2 rearranges to:

$$u = \sqrt{\frac{2K_e}{m}}$$  \hspace{1cm} \text{Equation 3}$$

Thus, from Newton's equation:

$$v = u + at$$  \hspace{1cm} \text{Equation 4}$$

where $v$ is the ion's velocity at the exit of the extraction region and $a$ is the acceleration of the ion in the extraction field. Substituting Equation 1 and 3 into Equation 4 gives:

$$v = \sqrt{\frac{2K_e}{m} + \frac{Eq}{m} TOF_x}$$  \hspace{1cm} \text{Equation 5}$$

where $TOF_x$ is the time of the ion X to move from its point of origin to the exit of the extraction region. Equation 5 rearranges to:

$$TOF_x = \frac{m}{Eq} \left[ v - \sqrt{\frac{2K_e}{m}} \right]$$  \hspace{1cm} \text{Equation 6}$$

Ion Y has the same initial kinetic energy as ion X but it is moving in the opposite direction. The field decelerates the ion and stops it after $t_b$. The field turns the ion around and it is accelerated again taking the same amount of time to return its point of origin, $t_b$. The motion of the ion through the remainder of the spectrometer is the same as for the forward moving ion, $TOF_x$. The time of flight of the backward moving ion from its point of origin to the exit of the extraction field is:

$$TOF_y = TOF_x + 2t_b$$  \hspace{1cm} \text{Equation 7}$$

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The time of flight for the backward moving ion from its point of origin to the turn around position found by substituting Equations 1 and 3 into Equation 4, as shown in Equation 8.

\[
0 = -\sqrt{\frac{2K_x}{m} - \frac{Eq}{m} t_b}
\]

Equation 8

where \( t_b \) is the time the ion takes to move from its point of origin to the turn around position. Equation 8 rearranges to:

\[
t_b = \frac{m}{Eq} \sqrt{\frac{2K_x}{m}}
\]

Equation 9

Substituting Equation 9 into Equation 7 gives:

\[
TOF_y = TOF_x + \frac{2m}{Eq} \sqrt{\frac{2K_x}{m}}
\]

Equation 10

The difference in the time of flight of ion X and ion Y, \( \Delta t \), shown on Figure A1(b) is:

\[
\Delta t = TOF_y - TOF_x
\]

Equation 11

Substituting Equations 6 and 10 into Equation 11 gives:

\[
\Delta t = \frac{2m}{Eq} \sqrt{\frac{2K_x}{m}}
\]

Equation 12

Equation 12 rearranges to:

\[
K_x = \frac{1}{8} \left( \frac{q^2}{m} \right) E^2 \Delta t^2
\]

Equation 13

Thus, the initial kinetic energy of the dissociating fragment ions can be found from Equation 13.
Appendix 3:

Visual Basic program designed to predict the time of flight of the ions in the TOF mass spectrometer and to predict the angular acceptance of the spectrometer for ions of a specified energy.

![TOF calculation program for mass spectrometer (11/9/96)](image)

**Figure A3:** Form 1 of the TOF simulation explained in this appendix. Definitions of the labels shown on the graph (picture 1) can be found in the program.

**FORM 1 CALCULATIONS**

Click on the CALC button

Sub cmdCalc_Click()

Defining the variables

Dim tsmal As Double
Dim tsbig As Double
Dim q1 As Double
Dim m1 As Double
Dim tp As Double
Dim bt As Double
Dim smdll As Double
Dim d1 As Double
Dim so1 As Double
Dim sfield As Double
Dim acc1 As Double
Dim I As Integer
Dim t1 As Double
Dim v1 As Double
Dim v2 As Double
Dim t2 As Double
Dim tt3 As Double
Dim xpos As Double
Dim ypos As Double

Setting up variables to store the values from the calculation

picture1.Cls
tsmal = 1000
tsbig = 0

Defining the labels along the x-axis (time axis) of picture 1

label(1) = 0
label(2) = Val(so.Text) / 2
label(3) = Val(so.Text)

Converting the chosen text values into SI units

ql = 1.6E-19 * Val(q.Text)
ml = 1.66E-27 * Val(mas.Text)
el = 1.6E-19 * Val(E.Text)
tp = Val(Tpl.Text)
bt = Val(btl.Text)
sol = Val(so.Text) / 100
smldl = Val(smald.Text) / 100
dl = Val(dText) / 100

Defining and calculating the applied electric fields

sfield = -1 * (tp - bt) / sol
acc1 = -1 * (Val(acc.Text) - tp) / smld1

Storing all TOF values for the 1000 positions across the source region

For i = 0 To 1000
    t1 = Sqr((2*ml*sol*i /1000)/(ql*sfield))
    v1 = sfield * ql * t1 / ml
    v2 = Sqr(v1^2+2*acc1*ql*smldl/ml)
    t2 = (v2 - v1) / (acc1 * ql / ml)
    tt3 = (dl / v2)
    ts(i) = 1000000 * (tt3 + t2 + t1)
    If tsbig < ts(i) Then tsbig = ts(i)
    If tsmal > ts(i) Then tsmal = ts(i)
Next i
Defining the picture 1 size and labels on y-axis (TOF)

\[
\text{drawwidth} = 2 \\
\text{label}(4) = \text{tsmal} \\
\text{label}(5) = (\text{tsbig} + \text{tsmal}) / 2 \\
\text{label}(6) = \text{tsbig} \\
\text{T3} = \text{ts}(500)
\]

Label at minimum on y-axis
Label at halfway point on y-axis
Label at maximum on y-axis

Putting all stored ts(i) values into picture 1

For i = 0 To 1000
    \[
    \text{xpos} = \text{picture1.ScaleWidth} / 1000 * i \\
    \text{ypos} = \text{picture1.ScaleHeight} - (\text{picture1.ScaleHeight} * (\text{ts(i)} - \text{tsmal}) / (\text{tsbig} - \text{tsmal}))
    \]
    \[
    \text{picture1.PSet} \ (\text{xpos}, \ \text{ypos}), \ &\text{HFF}
    \]
Next i

Load form2
form2.Show

**Figure A4:** Form 2 of the TOF simulation explained in this appendix. Definitions of the labels shown on the graph (picture 2) can be found in the program.

**FORM 2 CALCULATIONS**

Click on the SYM button

Sub Command3_Click ()

Defining the variables

Dim cs As Double
Dim tsmal As Double
Dim tsbig As Double
Dim csmax1 As Double
Dim csmax2 As Double
Dim tw As Double
Dim T3 As Double
Dim amax As Double
Dim tmmax As Double
Dim so3 As Double
Dim q1 As Double
Dim ml As Double
Dim e1 As Double
Dim vin As Double
Dim tp As Double
Dim bt As Double
Dim smld1 As Double
Dim d1 As Double
Dim so1 As Double
Dim detw2 As Double
Dim sfield As Double
Dim acc1 As Double
Dim i As Integer
Dim sig As Double
Dim fi As Double
Dim sign As Double
Dim so4 As Double
Dim inan As Double
Dim ang As Double
Dim vcomp As Double
Dim dist As Double
Dim v1 As Double
Dim t1 As Double
Dim v2 As Double
Dim t2 As Double
Dim tt3 As Double
Dim tt4 As Double
Dim i2 As Integer
Dim adown As Double
Dim aup As Double
Dim tih As Double
Dim til As Double
Dim xpos As Double
Dim ypos As Double

Setting up variables to store the values from the calculation

ReDim cs(1000)
picture2.Cls
scalemode = 3
drawwidth = 2
tsmal = 1000
tsbig = 0
cs = 0
csmax1 = 1
csmax2 = 1
Defining labels on the x-axis (TOF axis)

\[ tw = \text{Val}(\text{gwidth.Text}) / 2 \]
\[ T3 = \text{form1.T3} \]
\[ \text{label}(8) = T3 \]
\[ \text{label}(7) = T3 - tw \]
\[ \text{label}(9) = T3 + tw \]
\[ \text{amax} = 0 \]
\[ \text{tmax} = 0 \]

Convert the chosen text values into SI units

\[ \text{so3} = \text{Val}(\text{so2.Text}) / 100 \]
\[ q1 = 1.6 \times 10^{-19} \times \text{Val}(\text{form1.q.Text}) \]
\[ m1 = 1.66 \times 10^{-27} \times \text{Val}(\text{form1.mas.Text}) \]
\[ e1 = 1.6 \times 10^{-19} \times \text{Val}(E.\text{Text}) \]
\[ \text{vin} = \sqrt{2 \times e1 / m1} \]
\[ \text{tp} = \text{Val}(\text{form1.Tp1.Text}) \]
\[ \text{bt} = \text{Val}(\text{form1.bt1.Text}) \]
\[ \text{smld1} = \text{Val}(\text{form1.smald.Text}) / 100 \]
\[ \text{d1} = \text{Val}(\text{form1.D.Text}) / 100 \]
\[ \text{sol} = \text{Val}(\text{form1.so.Text}) / 100 \]
\[ \text{detw2} = \text{Val}(\text{dwth.Text}) \]

Defining and calculating the applied electric fields

\[ \text{sfield} = -1 \times (\text{tp} - \text{bt}) / \text{sol} \]
\[ \text{accl} = -1 \times (\text{Val}(\text{form1.Acc.Text}) - \text{tp}) / \text{smld1} \]

Random generation of a negative or positive sign

\[ \text{For} \ i = 0 \ \text{To}\ \text{sym1} \]
\[ \text{sig} = \text{so3} / (2.3555) \]
\[ \text{fi} = \text{Rnd} \]
\[ \text{sign} = \text{Rnd} \]
\[ \text{If} \ \text{sign} > 0.5 \ \text{Then} \ \text{sign} = -1 \ \text{Else} \ \text{sign} = 1 \]
Generation of a Gaussian distribution of ion position within the source region

\[
so4 = sl/2 + sign*(so3/2 - Sqr(-1*Log(fi)*2*sig^2))
\]

so4 = distance from the top extraction plate to the ion position in the source.

\[
so4 = \frac{so1}{2} + \left( \frac{so3}{2} - \sqrt{-2\log(fi)(sig)^2} \right)
\]

If so4 < 0 Then GoTo 100

Generation of the isotropic angular distribution for ions from source region

\[
inan = Rnd
ang = Atn(-1 * inan / Sqr(-1 * inan * inan + 1)) + 1.5708
\]

Random generation of forward or backward direction moving ion wrt to the detector

sign = Rnd
If sign > .5 Then ang = 3.1415926 - ang

Determination of the component of velocity of ion along the detector axis

\[
vcomp = vin * \cos(\text{ang})
\]

Calculation of distance to the ion turnaround point in the extraction region

\[
dist = \frac{vcomp^2}{2 \times \text{sfield} \times q1 / m1}
\]

From Newtons equation:

\[
v^2 = u^2 + 2as
\]

where \(u=0\) in this case.

Determining whether the ion is lost (if it hits the bottom extraction plate before the field turns it around)

If vcomp < 0 Then If dist > (so1 - so4) Then GoTo 100

Calculation of the total TOF of the ion in the TOF mass spectrometer

\[
v1 = \sqrt{vcomp^2 + 2 \times \text{sfield} \times q1 \times (so4)/m1}
\]

\(v1\) = velocity of ion at exit to extraction region calculated from \(v^2 = u^2 + 2as\)

\[
t1 = \frac{v1 - vcomp}{\text{sfield} \times q1 / m1}
\]

\(t1\) = time in extraction region

\[
v2 = \sqrt{v1^2 + 2 \times \text{acc1} \times q1 \times \text{sml} / m1}
\]

\(v2\) = velocity at the exit to the accel. region

\[
t2 = \frac{v2 - v1}{\text{acc1} \times q1 / m1}
\]

\(t2\) = time in acceleration region
$tt3 = \frac{d1}{v2}$ $tt3= \text{time in drift region}$

$tt4 = 1000000 \times (tt3 + t2 + t1)$ $tt4= \text{total TOF (µs)}$

Scaling the flight time to the channel number

\[i2 = \text{Int}(1000 \times (tt4 - (T3 - tw)) / (2 \times tw))\]
\[\text{If } i2 > 1000 \text{ Then GoTo 100}\]
\[\text{If } i2 < 1 \text{ Then GoTo 100}\]

Determination of the maximum angular acceptance of the spectrometer for the ion and whether it is for ions initially moving away from or towards the detector

\[\text{If } ((\text{detw2} - (tt4 \times \text{vin} \times \text{Sin(ang)} / 1000000))^2)^{.5} < (\text{detw2} / 100) \text{ Then}\]
\[\text{amax} = \text{ang}\]
\[\text{amax} = \text{maximum acceptance angle}\]

\[\text{If } \text{amax} > 1.5708 \text{ Then } \text{adown} = \text{amax} \text{ Else } \text{aup} = \text{amax}\]

\[\text{adown} = \text{maximum accep. angle for ions moving initially away from the detector}\]
\[\text{aup} = \text{maximum accep. angle for ions moving initially towards the detector}\]

\[\text{If } tt4 \times \text{vin} \times \text{Sin(ang)} / 1000000 > \text{detw2} \text{ Then GoTo 100}\]

Determination of the peak position for the ions moving initially toward and away from the detector

\[cs = cs + 1\]
\[\text{If } (i2 < 500) \text{ And } (cs > \text{csmax1}) \text{ Then}\]
\[tih = i2\]
\[\text{tih= the time of the peak of the backward moving ion peak}\]

\[csmax = cs\]
\[\text{ElseIf } (i2 > 500) \text{ And } (cs > \text{csmax2}) \text{ Then}\]
\[til = i2\]
\[\text{til= the time of the peak of the forward moving ion peak}\]

\[csmax = cs\]

End If
Converting calculated TOF and so1 value into the dimensions of the picture2

```vbnet
xpos = picture2.ScaleWidth / 1000 * i2
ypos = picture2.ScaleHeight - picture2.ScaleHeight * cs / ht1
picture2.Line (xpos, picture2.ScaleHeight)-(xpos, ypos), &HFF
```

ht1=y-counts text box

100 Next i

Defining the labels on x-axis (TOF) for picture 2

```vbnet
label(11) = (til / 1000) * tw * 2 + (T3 - tw)
label(10) = (tih / 1000) * tw * 2 + (T3 - tw)
```

Defining the acceptance angles for a forward and a backward moving ion

```vbnet
label(12) = (aup / 3.1415926) * 180
label(13) = (3.1415926 - adown) / 3.1415926 * 180
```

End Sub
Appendix 4

Calculation of the TOF of ions with an initial kinetic energy from their point of origin to the detector.

The extraction field is expressed as $E_x$ and the acceleration field as $E_a$. The distance of the ion point of origin to the exit of the extraction field is given as $d_x$, the total acceleration field distance as $d_a$ and the total drift region distance as $d_d$. The time the ion takes to move from its point of origin to the exit of the extraction region is $t_x$. The time the ion takes to move from the entrance of the acceleration region to the exit is $t_a$ and the time the ion takes to move from the entrance of the drift region to the exit is $t_d$.

![Diagram of TOF mass spectrometer](Image)

**Figure A5:** The dimensions of the TOF mass spectrometer used in the calculations in this appendix.

The calculation describes the movement of an ion towards the detector but the same method can be used for ions moving away from the detector. The calculations use the following equations:

\[ F = ma \quad \text{and} \quad a = \frac{Eq}{m} \quad \text{Equation 1} \]

where $E$ is the electric field and $q$ and $m$ are the mass and charge of the ion respectively.
The motion of the ion in the extraction region:

The initial velocity of the ion is determined from its initial kinetic energy, \( K_e \):

\[
K_e = \frac{1}{2}mu^2 \quad \text{Equation 2}
\]

which rearranges to:

\[
u = \sqrt{\frac{2K_e}{m}} \quad \text{Equation 3}
\]

where \( u \) is the initial velocity, \( m \) is the mass and \( K_e \) is the initial kinetic energy of the ion.

The final velocity of the ion, \( v \), was found using:

\[
v^2 = u^2 + 2as \quad \text{Equation 4}
\]

Substituting Equations 1 and 3 into Equation 4 gives:

\[
v = \sqrt{\frac{2E_0qd_e}{m} + \frac{2K_e}{m}} \quad \text{Equation 5}
\]

The time taken for the forward moving ion to leave the extraction field can be found from:

\[
v = u + at \quad \text{Equation 6}
\]

Substituting Equations 1 and 5 into Equation 6 gives:

\[
\sqrt{\frac{2E_0qd_e}{m} + \frac{2K_e}{m}} = \frac{E_0qt_e}{m} + \sqrt{\frac{2K_e}{m}} \quad \text{Equation 7}
\]

which rearranges to:
\[ t_e = \frac{m}{E_a q} \left[ \sqrt{\frac{2E_e q d_e}{m}} \right] \]  \hspace{1cm} \text{Equation 8}

The motion of the ion in the acceleration region:

At the entrance to the acceleration region the ion is moving with the velocity that was calculated as the final velocity in the extraction region. Therefore the initial velocity:

\[ u = \sqrt{\frac{2E_e q d_e}{m} + \frac{2K_e}{m}} \]  \hspace{1cm} \text{Equation 9}

and the final velocity in the acceleration region can be calculated using Equation 4. Substituting Equation 1 and 9 into Equation 4 gives:

\[ v = \sqrt{\frac{2q}{m} \left( d_e E_e + d_a E_a \right) + \frac{2K_e}{m}} \]  \hspace{1cm} \text{Equation 10}

Substituting Equations 1 and 10 into Equation 6 gives:

\[ \sqrt{\frac{2q}{m} \left( d_e E_e + d_a E_a \right) + \frac{2K_e}{m}} = \sqrt{\frac{2E_e q d_e}{m} + \frac{2K_e}{m}} + \frac{E_a q}{m} t_a \]  \hspace{1cm} \text{Equation 11}

which rearranges to:

\[ t_a = \frac{m}{E_a q} \left[ \sqrt{\frac{2q(d_e E_e + d_a E_a) + 2K_e}{m}} - \sqrt{\frac{2E_e q d_e + 2K_e}{m}} \right] \]  \hspace{1cm} \text{Equation 12}

Considering the motion of the ion in the drift region:

There is no acceleration within the drift region. The velocity remains at the same value as at the exit of the acceleration throughout the ion's passage through this region.
The initial and final velocity is therefore:

\[ v = u = \frac{2q}{m} \left( d_s E_x + d_d E_a \right) + \frac{2K_e}{m} \]  

Equation 13

Using the simple equation \( t = \frac{s}{v} \), where \( s \) is the distance the ion travels in the drift region, and \( v \) is the ion's velocity, the time of flight of the ion through the drift region can be found:

\[ t_d = \frac{d_d}{\sqrt{\frac{2q}{m} \left( d_s E_x + d_d E_a \right) + \frac{2K_e}{m}}} \]  

Equation 14

The motion of the ion in the Time of Flight Mass Spectrometer:

The total time of flight of the forward moving ion in the TOF mass spectrometer can be found by summing the flight time of the ion within the three regions:

\[ T_t = t_e + t_a + t_d \]  

Equation 15

Substituting Equations 8, 14 and 12 into Equation 15 gives:

\[ T_t = \frac{m}{E_{eq}} \left[ \sqrt{\frac{2E_{eq}d_e}{m}} \right] + \frac{m}{E_{aq}} \left[ \sqrt{\frac{2q}{m} \left( d_s E_x + d_d E_a \right) + \frac{2K_e}{m}} - \sqrt{\frac{2E_{eq}d_e}{m}} + \frac{2K_e}{m} \right] + \frac{d_d}{\sqrt{\frac{2q}{m} \left( d_s E_x + d_d E_a \right) + \frac{2K_e}{m}}} \]  

- Equation 16
which rearranges to:

\[
T_i = \sqrt{2} \frac{m}{q} \left[ \sqrt{\frac{d_x}{E_x}} + \sqrt{\frac{d_xE_x + d_xE_a + K_xq}{E_a}} - \frac{\sqrt{d_xE_x + K_xq}}{E_a} + \frac{d_d}{2\sqrt{d_xE_x + d_xE_a + K_xq}} \right]
\]

-Equation 17

Thus, if the kinetic energy (calculated from the velocity parallel to the TOF axis) equals 0 eV then plotting Time of Flight, \(T_i\), as the ordinate on a graph and \(\sqrt{\frac{m}{q}}\) as the abscissa produces a linear graph, as shown in Figure 2.13. This relationship shows no y-intercept. Thus any offset in the experimental results shows the delay in the electronics used in the detection and display of the spectra. An intercept is due to a difference between the time taken for the trigger pulse to travel from the laser to the MCS and the time taken for the ion signal to travel from the detector to the MCS.
Appendix 5

A spreadsheet has been designed in Quattro-Pro to determine the initial kinetic energy of the fluorine ions from the Coulomb explosion of SF₆ from the critical distance.

The critical distance is assumed to be 2.22 times the equilibrium distance for the atoms in the spherically symmetric SF₆ molecule, \( R_c = C_m^{-1} R_e \) where \( C_m \) is approximately 0.45 for light molecules such as CO, N₂ and O₂, from Posthumus et al, 1995.

The force on one of the fluorine ions, \( F_1 \), at the critical distance is calculated taking into account the five fluorine atoms, \( F_2-F_5 \), and the sulphur ion, \( S \).

![Figure A6: Sulphur hexafluoride molecule.](image)

From the force on the fluorine ion, \( F_1 \), due to the charges on the other ions, \( S \) and \( F_2-F_5 \), the velocity of \( F_1 \) is calculated at time = 0 and, hence, the distance it moved in a small increment of time (1 fs). However, the new force can then be calculated and the steps described above repeated until the force does not change significantly with each time interval. The temporal increments are increased to 10 fs and the calculations repeated at each incremental step until the force on \( F_1 \) does not change significantly for each increment of time. This process is repeated again for temporal increments of 100 fs. Finally, when the force on \( F_1 \) does not change for incremental steps of 100 fs the molecule is assumed to be dissociated (8925 fs for the \( F^+ + S^{2+} + F^3+ \) channel). The energy gained by the Fluorine ion, \( F_1 \), at the end of each increment of time is calculated by determining the product of the force and distance moved. The kinetic energies gained by \( F_1 \) at the end of each
increment of time are summed which gives the total energy of the fluorine ion, F1. 
The total kinetic energy of the dissociative ionization channel is found by adding the 
kinetic energies of all six fluorine ions together.

This calculation can only be used for symmetric dissociative ionization channels 
since it relies on the fact that the opposite fluorine ions expand the same distance 
by the end of each time interval.
Appendix 6:

Glossary

ADK (Ammosov-Delone-Krainov) theory: Quasi-classical ac tunneling model that predicts ionization rates of complex atoms.

Appearance intensity: The laser intensity at which 10 ions per pulse are detected (Augst et al, 1991)

Keldysh parameter, $\gamma$: Defines the boundary between multiphoton ionization and very intense field ionization, otherwise known as tunneling.

\[
\gamma = \frac{\omega_L}{\omega_{\text{run}}} = \sqrt{\frac{E_0}{2U_p}} = \frac{\omega_L}{eE_0} \sqrt{2mI_0}
\]

where $\omega_L$ is the angular frequency of the optical field, $\omega_{\text{run}}$ is the tunneling rate through the barrier at the peak of the optical field, $E_0$ is the field free binding energy of the electron, $U_p$ is the Ponderomotive potential, $e$ and $m$ are the charge and mass of an electron respectively and $I_0$ is the ionization energy of the atom.

Keldysh theory: Calculates perturbatively the transition rate from an initial bound state to a free electron oscillating in the laser field (a non-perturbative Volkov final state).

Laser pulse rise time: The time over which the intensity of the laser pulse rises from zero to the peak laser intensity.

Laser induced states: Virtual states, with a lifetime determined by the Heisenberg Uncertainty principle, which only occur in the presence of the laser field. The energy separation of the states is determined by the energy of the photons in the laser field.

MEDI process: Multi-Electron-Dissociative-Ionization. A process where a molecule looses several electrons rapidly and the molecular ions explode into energetic fragment ions.

Peak laser intensity: The maximum in the temporal and spatial distribution of the laser pulse.
**Ponderomotive potential:** The time averaged kinetic energy of a free electron oscillating in an ac field.

**Saturation intensity:** The laser intensity at which the depletion of the neutral species takes place.

**Szőke’s modified Keldysh theory:** Superimposes the constant molecular potential and the oscillating electric field in the calculation of the final Volkov state.
Appendix 7:

Posters presented at Conferences

XX ICPEAC Vienna, Austria, 1997 - High intensity laser fragmentation of vibrationally excited CO$_2$ (Tu 032).

Multi-electron dissociative ionization of SF$_6$ in high intensity femtosecond laser pulses (Tu033).

ATMOP XXII Oxford, UK 1996 - Multi-electron interactions with CO.


XIX ICPEAC Vancouver, Canada 199 - Multiphoton interactions with CO$_2$ and N$_2$O.
Multielectron-dissociative-ionization of SF\(_6\) by intense femtosecond laser pulses

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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 \textit{et al} 1992), or in collisions between high-energy molecular ions and a foil target (Vager \textit{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 (Hitchcock \textit{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 \textit{et al} 1996). More recently, large complex molecules and clusters have also been subjected to femtosecond laser pulses (Ledingham \textit{et al} 1995, Shao \textit{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\(^{-2}\).
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 $\pm 5\%$ 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 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 $\pm 5$ fs.

Taking into account the pulse energy of 60 $\mu$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$_6^+$ ions are observed, the most massive fragment ion being SF$_5^+$. 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$_5^+$,
Multielectron-dissociative-ionization of SF$_6$

Figure 1. TOF spectrum for SF$_6$ recorded at $7 \times 10^{15}$ W cm$^{-2}$ with an extraction field of 300 V cm$^{-1}$, (a) with the laser polarization direction parallel, and (b) with the polarization perpendicular to the spectrometer axis. In the case of S$^{3+}$ and S$^{4+}$ the fragment positions are marked, but the fragments are obscured by the F$^{3+}$ forwards and backward ions.

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$_6^{5+}$ 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$_4^{2+}$ and SF$_2^{2+}$, indicates that the parent ion has been doubly charged. The formation of SF$_6^{5+}$ also leads to DDI in which SF$_2^{2+}$ dissociates into two fragment ions typically SF$_4^{n+}$ 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$_2^+$, because the pulse length of 60 fs is short with respect to the dissociation timescale of SF$_6^{5+}$. 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$^{4+}$ and S$^{3+}$ 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\(_3^+\), 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\(_3^+\) 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\(^{3+}\) 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\(_3^+\) 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 \(et\ al\) (1994) and Codling \(et\ al\) (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 \(et\ al\) 1978) and MEDI and two
Multielectron-dissociative-ionization of SF₅

Figure 3. TOF spectra for SF₅ 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.

Table 1. Observed Coulomb explosion fragment ions of SF₅.

<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>

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 SF₅.
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 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>$S^{3+}$</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>47.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S^{6+}$</td>
<td>72.68</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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, $R_c = C_m^{-1}R_e$, 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 3. Possible Coulomb explosion fragmentation channels of SF$_6$ and calculated Coulomb energies for $R_0 = 3.51$ 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$_6^{+}$ → S$^+$ + 6F$^+$</td>
<td>66</td>
<td>F$^+$ (11)</td>
</tr>
<tr>
<td>(2) SF$_6^{+}$ → S$^{2+}$ + 6F$^+$</td>
<td>90.6</td>
<td>F$^+$ (15.1)</td>
</tr>
<tr>
<td>(3) SF$_6^{2+}$ → S$^{3+}$ + 6F$^{2+}$</td>
<td>262.8</td>
<td>F$^{2+}$ (43.8)</td>
</tr>
<tr>
<td>(4) SF$_6^{3+}$ → S$^{4+}$ + 6F$^{2+}$</td>
<td>312</td>
<td>F$^{2+}$ (52)</td>
</tr>
<tr>
<td>(5) SF$_6^{4+}$ → S$^{4+}$ + 6F$^{2+}$</td>
<td>361.2</td>
<td>F$^{2+}$ (60.2)</td>
</tr>
<tr>
<td>(6) SF$_6^{5+}$ → S$^{3+}$ + 4F$^{2+}$ + 2F$^{3+}$</td>
<td>393.6</td>
<td>F$^{2+}$ (54.1) F$^{3+}$ (88.6)</td>
</tr>
<tr>
<td>(7) SF$_6^{6+}$ → S$^{4+}$ + 4F$^{2+}$ + 2F$^{3+}$</td>
<td>451.2</td>
<td>F$^{2+}$ (62.3) F$^{3+}$ (101)</td>
</tr>
<tr>
<td>(8) SF$_6^{7+}$ → S$^{5+}$ + 4F$^{2+}$ + 2F$^{3+}$</td>
<td>508.6</td>
<td>F$^{2+}$ (70.5) F$^{3+}$ (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 $R_0$, we assume that $C_m$ is 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$^{-2}$ 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 unaligned 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 x 10$^{15}$ W cm$^{-2}$, is at least a factor of eight times higher than the intensity at which these ions appear (8 x 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 x 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 $\text{SF}_4^-$ 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 $\text{SF}_4^-$ in figure 3, also it is reasonable to expect that the $\text{SF}_4^-$ 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.

References


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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$^{2+}$ 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 Cornaggia et al (1994) and Cornaggia (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...
Letter to the Editor

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).

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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 CO₂, 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 CO₂ present is shown in figure 2, in which the prominent contamination features H₂O⁺, OH⁺, O⁺ and O²⁺ are detected. These features arise from

![Figure 1. TOF spectrum for CO₂ recorded at room temperature and 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 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$^{3+}$ 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 CO₂ initially in the ground state the O⁺ + C⁺ + O⁺ channel is aligned with the laser field such that a model distribution of angles θ (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 CO₂ 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 (θ = 90°). If this is the case the CO₂ molecule will then tend to bend further, decreasing the bend angle γ. 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 θ = 90°, the equilibrium C-O bond length of 1.16 Å is constant, and that the C⁺ ions result from the

Figure 3. Kinetic energy distribution; (a) C⁺, (b) C²⁺ and (c) C³⁺ fragment ions derived from the forward portion of the room temperature and 200°C TOF spectra.
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\(^+\) 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\(^{3+}\) channel, which is higher than observed. It seems that the higher stages of ionization result from only the well aligned molecules.
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 θ = 90°.

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References

Herzberg G 1945 Molecular Spectra and Molecular Structure vol 2 Infrared and Raman Spectra of Polyatomic Molecules (New York: Van Nostrand) p 172
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 Comaggia.

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 (Comaggia 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 a 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 × 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 × 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$_2$ 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$^+$ ion distribution peaked along the polarization direction and secondly the molecules are bent at the time of the Coulomb explosion giving the C$^+$ 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$^+$. Considering the O$^+$ angular distribution in more detail by displaying the O$^+$ 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$^n$(θ) 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$^n$(θ) 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.
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Table 1. Parameters derived from the least-squares fit of $A \cos^n(\theta)$ 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 ($2 \times 10^9$ 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 bonds stretch 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 $\alpha_\parallel$ and perpendicular $\alpha_\perp$ to the internuclear axis is given by the expression

$$V_a(\theta) = -\frac{1}{2} \varepsilon^2 (\alpha_\parallel \cos^2(\theta) + \alpha_\perp \sin^2(\theta))$$

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 $\alpha_\parallel : \alpha_\perp$ 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 $\alpha_\parallel : \alpha_\perp$ 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 $\alpha_\parallel$ 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 $\alpha_\parallel$ 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 $\alpha_\parallel$ and $\alpha_\perp$ are already quite close in magnitude (Bhardwaj et al 1997), where as
for an initially linear molecule $\alpha$ 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. Angular distribution of O$^+$ ions predominantly from the (1,2,1) channel. When $\theta$ is zero the TOF axis is parallel to the laser direction. The curve is an $A \cos^n \theta$ least-squares fit (see table 1) and the straight lines are the triangular distribution derived from the double-correlation map by Cornaggia (1996).](image-url)
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![Graph showing angular distribution of ions](image)

Figure 5. Angular distribution of O^{3+} 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.

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References

Spatial alignment of molecules by intense, linearly-polarized light fields and the effects of space charge

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Abstract

Angular distributions are measured of \( S^+ \) and \( S^{2+} \) fragment ions formed by dissociative ionization of \( \text{CS}_2 \) by intense \((10^{13} \text{ W cm}^{-2})\), 532 nm laser pulses of 35 ps duration. Pronounced anisotropies are observed which are indicative of the degree of spatial alignment of the precursor molecules along the direction of the laser polarization vector. Measurements made under different target-density conditions indicate that space charge and laser intensity are two factors which determine the "tightness" with which field-induced spatial alignment of molecules is achieved. © 1998 Elsevier Science B.V.

Large dipole moments induced in molecules by intense, linearly polarized light fields exert torques which can swamp rotational motion, and can result in spatial alignment of linear molecules such that their internuclear axes point along the direction of the light polarization vector. Signatures of such spatial alignment are obtained in experiments which measure the angular distributions of fragment ions produced when molecules undergo dissociative ionization due to interaction with intense, linearly polarized laser radiation.

The most significant implication of the field-induced dipole moment is that the molecules may be "trapped" in pendular states which are aligned about the field polarization axis, giving rise to structured, anisotropic distributions of the products of dissociative ionization (DI). Experimental evidence for the preferential alignment of the internuclear axes of molecules along the polarization axis of linearly polarized laser beams has been obtained in measurements of angular distributions of fragment ions produced in intense-field-induced DI experiments on diatomic molecules [1-3], triatomics molecules possessing both linear [4,5] as well as bent [6] geometries and polyatomic molecules [7,8]. Friedrich and Herschbach [9] have shown theoretically that pendular states which arise out of laser-field-induced dipole moments are directional superpositions of field-free molecular states, corresponding to oblate spheroidal wavefunctions whose eigenenergies decrease with increasing field strength. Experimental manifestation of field-induced pendular motion has been recently demonstrated in the case of \( \text{CO}_2 \) and \( \text{CS}_2 \) molecules [4,5].

The formation of spatially aligned molecules broadens the horizons for spectroscopy [10] and chemical reaction dynamics [11] as well as being of intrinsic interest in studies of laser–matter interac-
It is, therefore, of interest to explore limitations which might be imposed on the dynamics of the spatial alignment process by the nature of the laser–molecule interaction. Specifically, we address in the present study the question: does the field-induced alignment get disturbed by effects induced by the space charge in the intense plasma that is created in the laser–molecule interaction zone?

It has been shown by Delone and Krainov [12], in the context of the ionization of atoms in intense laser fields that space charge effects can give rise to significant distortions of the initial angular and energy distributions of both atomic ions and ejected electrons which are formed in the focal zone of an intense laser beam. Ammosov et al. [13] developed a model describing these effects. As the laser field induces atomic ionization, some (or all) of the ionized electrons leave the space which was occupied by the atoms. As a result, a net positively-charged space is created. The remaining ion volume expands, driven by coulombic repulsion. Such expansion causes distortions in the initial ion distribution and gives rise to complicated dynamics as the interaction between the electrons and the ion volume retards the electrons and, consequently, alters their trajectories. Whereas manifestations of such space charge effects have been unambiguously observed in electron motion (particularly in above-threshold ionization spectra [13]), the complex dynamics of ion motion has so far precluded corresponding observations in the ion channels.

Effects of space charge saturation on ion angular distributions are explored in the present study by conducting DI experiments on the linear triatomic, carbon disulfide, at a wavelength of 532 nm and at laser intensities of the order $10^{13}$ W cm$^{-2}$, using two different laser–molecule interaction geometries. A description of the apparatus has been presented recently [14] and, therefore, only the salient features are outlined here. A schematic representation of the experimental arrangement is shown in Fig. 1. Focussed, linearly-polarized, 35 ps wide, 532 nm light pulses, obtained from an Nd:YAG laser (where Nd:YAG denotes neodymium-doped yttrium aluminum garnet), interacted with the molecules of interest in a chamber pumped to a base pressure of ~ 10$^{-7}$ Torr using a large (2500 l s$^{-1}$) diffusion pump. In one version of the laser–molecule interaction geometry, a molecular beam source was utilized which presented the focussed laser beam with a molecular target of radius ~ 1 mm. The gas pressure within such a target ($10^{-9}$ - $10^{-7}$ Torr) corresponded to a number density of $10^{10}$ - $10^{11}$ cm$^{-3}$. In another version, the molecular beam was replaced by an effusive gas source which provided a diffuse molecular target; the pumping geometry employed ensured target gas pressures ($1-3 \times 10^{-5}$ Torr) which corresponded to considerably smaller number densities ($\leq 10^{4}$ cm$^{-3}$). The laser spot size used in conjunction with both targets was of the order of 100 µm in diameter and it is estimated that there were ~ 1000 molecules in the laser–molecule interaction volume when experiments were conducted in the diffuse target geometry. The repetition rate of our laser was 10 Hz and, at saturation intensity (the laser intensity at which 100% ionization is expected to occur) expected ion count rates of ~ $10^{12}$ s$^{-1}$ were obtained. Assuming a spherical laser–molecule interaction volume, the Coulomb interaction between ions would give rise to a distribution of kinetic energies ranging from a minimum value of the order of 1 cm$^{-1}$ (for two ions separated by a distance of ~ 100 µm) to a maximum value of 14.4 eV (for two ions separated by 1 Å).

Ions formed in the laser–molecule interaction were mass analyzed by means of a quadrupole mass spectrometer. Mass-selected ion intensities were mea-
sured by a channel electron multiplier (CEM) operating in the particle counting mode. The CEM was coupled, through conventional fast pulse counting electronics. Ion angular distributions were measured by rotating the polarization direction of the incoming laser field with respect to the spectrometer axis; a combination of half-wave plate and linear polarizer was used to obtain the desired polarization at constant intensity. The polarization direction was rotated in steps of 1–5°. In the course of several weeks’ of measurements, we found that the shot-to-shot reproducibility of the laser varied between ±5% and ±20%. In most of the present experiments, on-line monitoring of the shot-to-shot laser intensity was carried out and a trigger was provided to the digital oscilloscope only for those laser shots for which the intensity was within the figure of ±2.5% or ±5%. This was achieved using the gate-and-delay generator and counters shown in Fig. 1; counter B was used to indicate the number of laser shots, counter A indicated the gated ion counts whereas counter C indicated the ungated ion counts. The ratio of counts A/B yielded the gated count rate whereas the ratio A/C yielded the ungated count rate. As discussed below, we found that shot-to-shot variations in laser intensity could also play a role in determining the overall shape of the angular distribution function for fragment ions produced upon the DI of CS₂.

As in earlier experiments, our measurements were made without the use of an electrostatic field to extract ions from the laser–molecule interaction zone into the mass filter. It is established that in experiments in which a quadrupole mass spectrometer is used, even relatively weak extraction fields can severely distort angular distributions of singly-charged ions [4]. In our case, only those ions whose initial velocity vector lay within the acceptance angle set by the entrance aperture of the mass filter were detected; the angular resolution in the present measurements was ±1.8° for the experiments conducted using the molecular beam geometry; the corresponding figure for the diffuse gas target geometry was ±4°.

Space charge saturation effects depend on the number density of charged particles produced in the laser–molecule interaction. Specifically, such effects are determined by plasma parameters which, in turn, are directly affected by (i) the gas number density, (ii) the laser intensity and (iii) the size of the laser–molecule interaction zone within which initial plasma formation occurs. We ensured that the focussed laser spot size remained constant in the course of our experiments and we measured the angular distributions of S⁺ and S²⁺ fragment ions produced in the laser-field-induced dissociative ionization of CS₂ at different gas target densities and laser intensities. These two fragment species are the focus of our attention for reasons of illustration. S⁺ constitutes the major ion in the fragmentation process [15] whereas the doubly-charged S²⁺ fragment, while it is one of the minor constituents in the mass spectrum, is nevertheless important from the viewpoint of the relatively large kinetic energy with which it is formed.

Fig. 2 shows polar plots depicting the angular distributions of S⁺ ions measured at three different laser intensities. In these plots the radial distance from the origin of each data point is a measure of ion intensity in a given angular direction. A number of angular distribution measurements were made which, taken together, covered all four quadrants in the angular range 0–360° around the mass spectrometer axis. As in other recent work reported from our laboratory, no difference was found in the shapes of the distributions obtained in the different quadrants when the alignment of the focussed laser beam with the molecular target was perfect. The angular distribution data depicted in Fig. 2 pertain to measurements made in the 0–90° quadrant; for clarity of presentation, we have chosen to reflect such single quadrant data over the 90–360° range. These data were measured under diffuse CS₂ pressure conditions which ensured a target number density which was in the range 10⁸–10⁸ cm⁻³.

We carried out measurements of S⁺ ion yield as a function of laser intensity over a wide range and our results indicate that even the highest laser intensity for which results are depicted in Fig. 2 lies considerably below the saturation intensity (Iₙsat) for this ion. Iₙsat is the value of laser intensity beyond which 100% ionization occurs and, for formation of S⁺ from CS₂, has been measured to be greater than 3 × 10¹⁵ W cm⁻² [16]. For angular distribution measurements conducted at laser intensities that are higher than Iₙsat, increase in the laser intensity would not affect the number of S⁺ ions that are produced.
and, consequently, space charge saturation effects would not be expected to come into play under such circumstances. Increasing the laser intensity may, however, lead to enhancement in the magnitude of the induced dipole moment and, as a result, on the “tightness” of the measured spatial distribution of $S^{1+}$ ions. At laser intensities that are below $I_{c}$, for $S^{1+}$ ions, space charge saturation effects are more likely to affect to dynamics which give rise to the measured angular distributions. For purposes of illustration we focus attention on the panels in Fig. 2 which show the angular distributions measured at laser intensities of $1.5 \times 10^{13}$ and $1.8 \times 10^{13}$ W cm$^{-2}$ (left and centre panels of Fig. 2). In the former case measurements were made using counter C (see Fig. 1) and the shot-to-shot laser intensity varied over the range $\pm 20\%$; in the latter case counter B was utilised to ensure that the laser intensity remained constant to within $\pm 5\%$ throughout the course of the measurements.

Both sets of data exhibit the pronounced anisotropy expected from considerations of DI of CS$_2$ molecules which are spatially aligned such that the S–C–S internuclear axes line up parallel to the laser polarization vector. The most striking feature of the marked anisotropy in both cases is the almost zero ion intensity obtained when the light polarization vector is orthogonal to the direction of our mass spectrometer. The lobe-like structure which is observed has been interpreted earlier [4,5] as a signature for the pendular motion of spatially aligned CS$_2$ precursors of the $S^{1+}$ ions; theoretical simulations were carried out in our earlier studies whose results provided support for such interpretation. In the present Letter, we wish to confine our attention to the gross features of the angular distributions and will not discuss the fine structure. It is clear that measurements made in the ungated mode, where the shot-to-shot laser intensity varied by as much as $\pm 20\%$ (left panel) gives rise to an angular distribution which is somewhat broader than the considerably “tighter” distribution measured when data acquisition is in the gated mode (middle panel). The right panel in Fig. 2 shows angular distribution data obtained using a higher laser intensity and this also produces a considerably broader distribution. An example of an angular distribution measured using a denser target is shown in Fig. 3 (in this case, a CS$_2$ molecular beam was used, where target number densities were considerably higher, $\sim 10^{11}$ cm$^{-1}$ but the laser intensity was almost the same as that used in acquiring data shown in Fig. 2).

Our measurements indicate that the broadness of the measured angular distribution function is strongly dependent upon the experimental conditions under which measurements are made. Earlier experiments in our laboratory [4] had shown that the presence of an ion extraction field was an important experimen-
Fig. 3. Angular distribution of $S^{2+}$ ions measured using a molecular beam target (see text) The laser intensity used in these measurements was $2.5 \times 10^{15} \text{ W cm}^{-2}$.

Fig. 4. Angular distributions of $S^{2+}$ fragment ions measured using the molecular beam geometry (left panel) and the diffuse target geometry (right panel). The laser intensity was almost the same in the two measurements. The $\cos^2 \theta$ and $\cos^5 \theta$ distributions shown in the two panels are indicative of the considerably "tighter" angular distribution obtained under diffuse target conditions.

Conducted below the saturation intensity for the ion species under investigation. Moreover, comparison of the angular distribution data shown in the middle and right panels of Fig. 2 indicates that, notwithstanding artifacts introduced by experimental constraints, as the laser intensity increases from $1.8 \times 10^{13}$ to $3 \times 10^{13} \text{ W cm}^{-2}$, the degree of "tightness" of the $S^{2+}$ angular distribution appears to lessen. As discussed below, we believe that such broadening is attributable to space charge effects. Increasing the laser intensity results in an expansion of the plasma volume over which DI processes occur and, perhaps more significantly, results in a higher charge density.

Attempts to quantify the degree of "tightness" have proved unsuccessful, particularly in the case of $S^{2+}$ ions where the measurements were particularly difficult because of low ion count rates (we discuss below the somewhat more favorable case of $S^{+}$ angular distributions). Measurements were conducted by us over a range of $\text{CS}_2$ pressures in the diffuse geometry. We found that the gross features of the angular distributions (anisotropic distributions, with some evidence of fine structure) remained essentially unaltered.
results are shown in Fig. 4 for a laser intensity of \(\sim 2 \times 10^{14} \text{ W cm}^{-2}\). Both sets of data again show pronounced anisotropic angular distributions. As was indicated by the results obtained for \(S^+\), although there appears to be little evidence of a qualitative change in the anisotropic nature of the angular distributions, there appear to be fairly profound differences in the fine structure which can be discerned in the angular distributions measured under the two conditions. In the molecular beam (higher target density) experiment, many measurements conducted over a range of \(\text{CS}_2\) pressures revealed that the \(S^+\) yield always exceeded zero at \(\theta = 90^\circ\), with the ratio of ion yields at \(\theta = 0^\circ\) and \(\theta = 90^\circ\) being \(\sim 15\). The corresponding ratio at \(\theta = 0^\circ\) and \(\theta = 50^\circ\) was \(\sim 2\). This is exemplified by the angular distribution being somewhat broader than that which would be expected on the basis of a \(\cos^2 \theta\) functional dependence expected by polarizability interaction (considering, in the lowest approximation, only the linear polarizability and ignoring the higher order terms, see Ref. [14] for more discussion). In the diffuse target experiments, however, the ratio of ion yields at \(\theta = 0^\circ\) to \(\theta = 90^\circ\) was infinity. The ion signal became zero at angles larger than \(\sim 70^\circ\). The \(S^+\) signal ratio at \(\theta = 0^\circ\) to \(\theta = 50^\circ\) was 30, fifteen-fold larger than in the higher target-density case. An alternative description is indicated in the right panel of Fig. 4, where a considerably "tighter" \(\cos^4 \theta\) distribution yields a better approximation to the gross features of the measured angular distribution than a \(\cos^2 \theta\) function. In this context it is pertinent to note that in practice, the laser intensity within the interaction volume in our experiments is not perfectly uniform. Various decay channels are likely to be important in different spatial regions of the focussed laser beam and, consequently, quantitative assignment of anisotropy parameters is not possible on the basis of present angular distribution measurements.

In summary, our data appears to provide qualitative (and perhaps some semi-quantitative) indications that laser-field-induced spatial alignment of molecules becomes "tighter" under diffuse target conditions. We reiterate at this juncture that the laser intensities used for acquiring the data shown in Fig. 4 were almost the same as those used to acquire the data shown in Fig. 3, as were the dimensions of the focussed spot. The only difference was in the number density of target \(\text{CS}_2\) molecules and, hence, on the initial density of the plasma created upon laser-\(\text{CS}_2\) interaction. It is also important to note that these types of measurements, made under zero-extraction-field conditions, are difficult, time consuming and prone to inaccuracies and these factors preclude quantitative assessment to be made of space charge effects at this juncture. However, in comparing the global features of the \(S^+\) and \(S^+\) angular distributions which we have measured using two different laser-molecule interaction geometries, we state with some certainty that space charge effects, along with laser intensity, probably constitute two of the most important factors which determine the "tightness" of fragment ions angular distributions which constitute the experimental signature of field-induced spatial alignment of molecules.

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References


References


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Keldysh, L. V. (1965) Sov. Phys. JETP 20 p1307


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