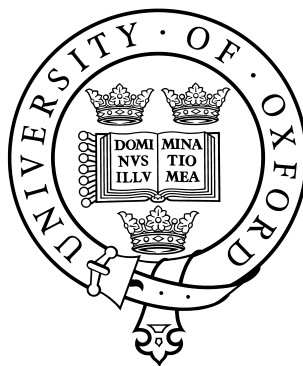


Laser Studies of Chemical Dynamics

A thesis submitted for the degree of Doctor of Philosophy

by

Alexander J. Gilchrist



Balliol College, University of Oxford

Trinity Term, 2013

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Abstract

In this thesis, resonance enhanced multiphoton ionisation (REMPI) in combination with time-of-flight mass spectrometry (TOF-MS) has been used to detect nascent photofragments resulting from the UV dissociation of a variety of small molecules. The translational anisotropy and angular momentum polarisation of these photofragments has been measured and used to elucidate the underlying photodissociation dynamics.

Firstly, the photodissociation of NO_2 at 320 nm has been investigated and the vector correlations of the nascent NO photofragments have been measured in terms of a set of semi-classical bipolar moments. The measured angular momentum alignment is found to be consistent with an impulsive model for the dissociation, with $\boldsymbol{\mu}$ and $\mathbf{v}$ in the same molecular plane and both preferentially perpendicular to $\mathbf{J}$, whilst angular momentum orientation measurements provide evidence for an additional torque due to the O–N–O bond opening during dissociation. These measurements were taken using a rotationally cooled, skimmed molecular beam and significant deviations were found between the bipolar moments measured using this source and previous measurements using a rotationally hotter source. The effect of parent molecular rotations on the measured bipolar moments has been quantified and successfully used to explain these deviations.

The photodissociation of Cl_2 has been studied in the wavelength region (320 – 350) nm. UV absorption in this wavelength region may result in two dissociation channels, $(\text{Cl} + \text{Cl})$ and $(\text{Cl} + \text{Cl}^*)$, and the angular momentum polarisation of both the $\text{Cl}(^2\text{P}_{3/2})$ and $\text{Cl}^*(^2\text{P}_{1/2})$ photofragments has been measured. This angular momentum polarisation has been reported in terms of a polarisation parameter formalism which, together with the measured translational anisotropies, has been

used to determine the different potential energy surfaces contributing to the dissociation process. Translational anisotropy measurements of the $\text{Cl}(^2\text{P}_{3/2})$ fragments have shown that, for the ground-state channel, dissociation results from a pure perpendicular transition to the C state, whilst alignment measurements show that non-adiabatic transitions to the A state are significant at large internuclear separations. The measured alignment parameters are found to be relatively constant for all dissociation wavelengths and are consistent with theoretical predictions. Translational anisotropy measurements of the $\text{Cl}(^2\text{P}_{1/2})$ photofragments show that, for the excited-state channel, dissociation occurs following a mixed parallel and perpendicular excitation to the B and C states respectively and the interference between these two dissociation pathways has been shown to result in angular momentum orientation.

The predissociation dynamics of the $\text{C } ^3\Pi_g (v = 0)$ and $(v = 1)$ Rydberg states of O_2 has been extensively studied. The translational anisotropy and angular momentum alignment of the $\text{O}(^3\text{P})$ and $\text{O}(^1\text{D})$ photofragments resulting from this predissociation has been measured in terms of a polarisation parameter formalism, which has been extended for a two-photon dissociation process. Measurements have been taken at various fixed wavelengths within the two bands in order to investigate the differences in the predissociation dynamics of intermediate levels with different values of $|\Omega| (= 0, 1, 2 \text{ in this case})$. The translational anisotropy is found to be dependent on the dissociation wavelength with the variations found to be consistent with rotational depolarisation due to the long lifetime of the excited C state. All photofragments have been found to be aligned, with the relationship between the measured $\text{O}(^3\text{P})$ and $\text{O}(^1\text{D})$ alignment being found to be consistent with a diabatic model of the dissociation. In addition, all photofragments are found to display coherent orientation resulting from interference between two possible two-photon absorption pathways. The measured orientation is affected by rotational depolarisation due to the long lifetime of the excited C state; once this effect is accounted for the orientation is found to be nearly constant over all dissociation wavelengths. The origin of the coherent orientation is attributed to two-photon absorption to different spin-orbit components of the C state.

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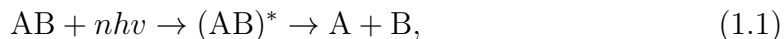
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Chapter 1

Introduction

1.1 Photodissociation dynamics

This thesis will focus on studying the photodissociation dynamics of small, gas phase molecules. The aim of this work is to determine the fundamental forces involved in the photodissociation process, whereby a bound molecule dissociates following the absorption of one or more photons to access an excited state, $(AB)^*$, and is formally defined for a diatomic molecule AB as,



where n is the number of absorbed photons and $h\nu$ is the energy of a photon with frequency ν . When studying a process of this type there are a number of key questions which an experimental or theoretical study will aim to answer. These will include the identity of the excited state $(AB)^*$, the finite lifetime of this state, the cause of this lifetime and the forces acting on the molecule as it dissociates.

The answer to many of these questions is primarily determined by the shape of the potential energy surfaces (PESs) of the molecule accessed during the dissociation process. A molecular potential energy surface is determined by solving the electronic Schrödinger equation within the Born-Oppenheimer approximation.¹ Within this approximation, the potential energy of a molecule may be determined for a fixed set

of nuclear coordinates and by determining how this potential energy changes with the geometry of the molecule a potential energy surface is constructed. For a diatomic molecule, this potential energy will simply be function of the internuclear separation, whilst for a polyatomic molecule the potential energy will be a multivariable function depending on all nuclear separations and bond angles.

Following the absorption of a photon with sufficient energy, the molecule may dissociate along these PESs *via* three main mechanisms which are illustrated in figure 1.1.¹ Firstly, the initial photon absorption may access a repulsive PES and the resulting repulsive force acting on the fragments will lead to rapid dissociation. This is known as *direct dissociation*. It is uncommon for dissociation to occur along just one repulsive PES and often dissociation will occur along multiple surfaces which will interact during the dissociation pathway. If the molecule is excited to a bound upper state then dissociation may still occur if this state is crossed by another repulsive state. This dissociation mechanism is referred to as Herzberg's type I or *electronic predissociation*² and the excited state lifetimes in this case will be longer than for a direct dissociation and determined by the strength of the coupling between the bound and repulsive PESs. A different type of predissociation, called Herzberg's type II or *vibrational predissociation*,² occurs when initial Franck-Condon excitation occurs to state with a minimum at small internuclear separations but has a barrier preventing direct dissociation. In this case, the initial states are quasi-stable and may dissociate by either tunneling through the barrier or by overcoming the barrier through internal vibrational redistribution (IVR) if more than two atoms are involved.

The identity and interactions between the various PESs involved in the dissociation pathway will affect many experimentally observable properties of the resulting photofragments. For example, there have been many studies of the scalar properties of the photofragments, which include the electronic excitation of the resulting fragments as well as their rotational and vibrational distributions.³ These product state distributions can provide a wealth of information on the dissociation process,

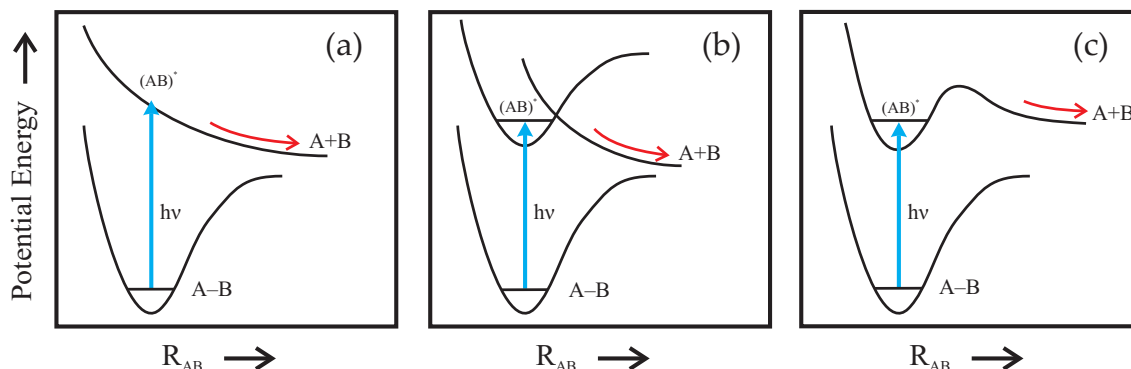


Figure 1.1: Illustrations of the three main photodissociation mechanisms, where (a) shows direct dissociation, (b) shows electronic predissociation and (c) shows vibrational predissociation. Adapted from Ref. 1.

often providing a very intuitive picture of the microscopic forces involved in the dissociation. One recent development in the studies of photodissociation dynamics, which may be identified through the measurement of photofragment rotational and vibrational distributions, is the roaming mechanism.⁴ This mechanism was first observed for the photodissociation of formaldehyde⁵ and has since been identified in the dissociation of other polyatomic molecules including acetone⁶ and the nitrate radical.⁷ In a traditional bond breaking mechanism, dissociation is characterised by a transition state in the form of a well-defined saddle point on the PES. A roaming mechanism, however, bypasses this transition state entirely and instead there is frustrated bond cleavage which leaves a part of the molecule without sufficient energy to escape. This fragment will orbit the remaining co-fragment until it encounters a reactive site and undergoes intramolecular abstraction.⁴ The photofragment product state distributions resulting from this mechanism will clearly be significantly different to that predicted by statistical theories which assume a traditional, tight transition state. For the dissociation of NO_3 at 588 nm, for example, two dissociation channels were observed with the vibrational and rotational photofragment distributions indicating that roaming occurs on both the ground and electronically excited surfaces.⁷ This thesis will, however, mainly focus on measuring the spatial properties of the dissociation process which, as will be shown in the next section, can

provide a sensitive probe of the anisotropic forces involved during dissociation and provides much new information to compliment that obtained from measurements of the scalar properties alone.

1.2 Vector correlations

The vectors which provide most information on the dissociation process are the photofragment recoil velocity, $\mathbf{v}$, the photofragment angular momentum vector, $\mathbf{J}$, and the transition dipole moment of the parent molecule, $\boldsymbol{\mu}$. The transition dipole of the parent molecules will be aligned in the space-fixed frame since, within the electric-dipole approximation, the probability that a molecule absorbs a photon is proportional to $|\boldsymbol{\epsilon}_{\text{phot}} \cdot \boldsymbol{\mu}|^2$, where $\boldsymbol{\epsilon}_{\text{phot}}$ is the electric vector of the dissociating light, so that the probability that a molecule will have an angle, θ , between $\boldsymbol{\epsilon}_{\text{phot}}$ and $\boldsymbol{\mu}$ is $\cos^2 \theta$. It is this space-fixed alignment of $\boldsymbol{\mu}$ that allows the measurement of the correlation between the other vectors of interest, $\mathbf{v}$ and $\mathbf{J}$, which will be discussed further in this section.⁸

1.2.1 Translational anisotropy

The most widely studied vector correlation is the translational recoil anisotropy arising between $\boldsymbol{\mu}$ and $\mathbf{v}$. For any parent molecule, there is a fixed angular correlation between the departing photofragment and the transition dipole moment. Therefore, if $\boldsymbol{\mu}$ is aligned in the space-fixed frame, there will also be an anisotropic distribution of $\mathbf{v}$. Zare and Herschbach⁹ determined that within the axial-recoil approximation, where the photofragment recoil velocity is assumed to be along the bond that breaks during the dissociation process, the angular distribution of photofragment recoil velocities, $I(\theta_\epsilon)$, will be given by,

$$I(\theta_\epsilon) = \frac{1}{4\pi}(1 + \beta P_2(\cos \theta_\epsilon)), \quad (1.2)$$

where $P_2(\cos \theta_\epsilon)$ is a second order Legendre polynomial¹⁰ and θ_ϵ is the angle between $\mathbf{v}$ and $\boldsymbol{\epsilon}_{\text{phot}}$. The parameter, β , describes the degree of recoil anisotropy and ranges from +2 for a transition where $\boldsymbol{\mu}$ is parallel to the dissociating bond to -1 where $\boldsymbol{\mu}$ is perpendicular to the dissociating bond. It is clear from equation (1.2) that these limiting values of β correspond to an angular distribution of photofragments which is proportional to $\cos^2 \theta_\epsilon$ and $\sin^2 \theta_\epsilon$, for $\beta = +2$ and -1 respectively, and is illustrated in figure 1.2.

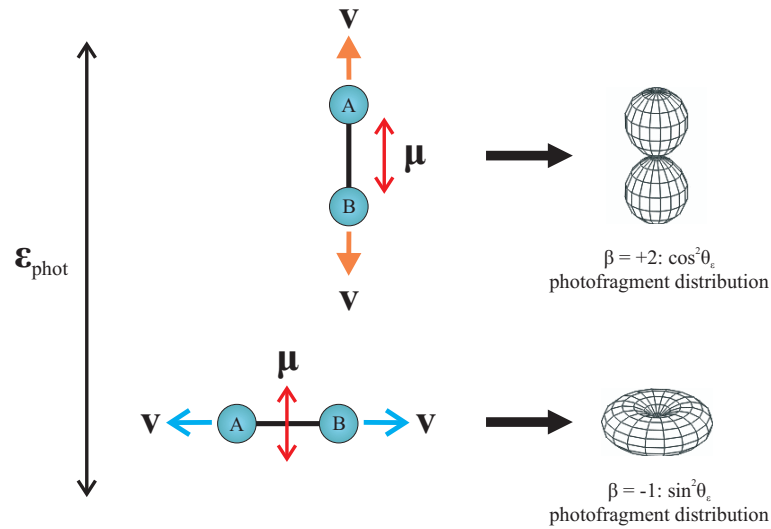


Figure 1.2: Illustrations of the angular distribution of the photofragment recoil velocity for a diatomic molecule AB following a pure parallel transition (top) and a pure perpendicular transition (bottom).

The limiting value that β takes will depend on the symmetry of the initially excited state and therefore measurements of the translational anisotropy primarily provide information on this symmetry. For a diatomic molecule undergoing a one-photon transition to a single excited state, $\boldsymbol{\mu}$ may either be parallel or perpendicular to the dissociating bond and therefore β will take a limiting value of either +2 or -1 respectively. For a polyatomic molecule, however, $\boldsymbol{\mu}$ may make an angle, χ , which lies between 0° and 90° to the dissociating bond axis and in this case the limiting value of β will be given by $2P_2(\cos \chi)$.

A reduction in the measured value of β from its limiting values may be due to a

number of reasons. Firstly, the photon absorption may be to multiple excited states and, if both parallel and perpendicular transitions are involved in the initial photon absorption, an intermediate value of β will be measured. Secondly, if the initially excited state is sufficiently long lived that rotational motion of the parent molecule in the time period between initial photon absorption and dissociation is significant then the initial $\cos^2 \theta$ alignment of the parent molecules (in the space-fixed frame) will be lost and a reduced translational anisotropy will be measured. This reduction in the measured value of β due to parent molecular rotations has been studied in a semi-classical model by Jonah and it is found that β will be reduced by a factor, β_{depol} , which is given by,¹¹

$$\beta_{\text{depol}} = \frac{1 + (\omega\tau)^2}{1 + 4(\omega\tau)^2}, \quad (1.3)$$

where ω is the angular frequency of the parent molecular rotation and τ is the average lifetime of the initially excited state, defined as the probability $(1/\tau)e^{-t/\tau}$ that a molecule dissociates in a time period t . Finally, equation (1.2) assumes axial-recoil and deviations from this will also lead to a reduction in the measured value of β . A tangential component to the recoil velocity may arise if the angular velocity of the parent rotation is fast compared to the recoil velocity along the breaking bond or, if a rotationally excited molecular fragment is produced, angular momentum conservation will require there to be an off-axis velocity component.¹² These causes of reduced translational anisotropy will affect measurements throughout this thesis and will be discussed in more detail in the relevant chapters.

1.2.2 Angular momentum polarisation

In addition to measurements of translational anisotropy, the spatial distribution of the photofragment angular momentum, $\mathbf{J}$, can also provide a considerable insight into the dissociation mechanism. Photodissociation may result in an anisotropic distribution of $\mathbf{J}$ which, for a molecular fragment, may mean that there is a preferred sense of rotation, either clockwise or anticlockwise, known as *orientation* or there is a preferred plane of rotation, known as *alignment*. The product angular momentum

orientation or alignment is described in terms of the distribution of $\mathbf{J}$ relative to a symmetry axis, z , with $\mathbf{J}$ described by the polar angles (θ, ϕ) with respect to this axis. For an ensemble of photofragment angular momenta, $\mathbf{J}$, the spatial distribution, $D(\theta, \phi)$, of these vectors may be expanded as a sum over the modified spherical harmonics, $C_q^k(\theta, \phi)$,^{10,13}

$$D(\theta, \phi) = \sum_{k=0}^{2J} \sum_{q=-k}^k A_q^{(k)}(J) C_q^k(\theta, \phi). \quad (1.4)$$

The moments of this expansion, $A_q^{(k)}(J)$, are called *polarisation parameters* and completely describe the spatial distribution of the photofragment angular momentum about the symmetry axis, z . If the system possesses cylindrical symmetry about z then only parameters with $q = 0$ are non-zero, however if this symmetry is broken the angular momentum distribution may potentially depend on a large number of parameters. Generally, polarisation parameters with odd- k describe the angular momentum orientation, whilst those with even- k describe the angular momentum alignment. In the high- J limit, where the angular momentum vectors may be treated classically, the three lowest order polarisation parameters with $q = 0$ are given by,

$$A_0^{(0)}(J) = 1, \quad (1.5)$$

$$A_0^{(1)}(J) = \langle P_1(\cos \theta) \rangle, \quad (1.6)$$

$$A_0^{(2)}(J) = 2 \langle P_2(\cos \theta) \rangle, \quad (1.7)$$

where $\langle P_k(\cos \theta) \rangle$ are ensemble averages of the Legendre polynomial of rank, k , in terms of $\cos \theta$. For an isotropic angular momentum distribution the only non-zero polarisation parameter is $A_0^{(0)}(J)$. If, however, the angular momentum is oriented or aligned then other polarisation parameters may take non-zero values. The $A_0^{(1)}(J)$ parameter is the lowest order parameter describing the angular momentum orientation and takes limiting values of $+1$ or -1 if the angular momentum is oriented parallel or antiparallel respectively to z . The $A_0^{(2)}(J)$ parameter is the lowest order

parameter describing the angular momentum alignment and takes limiting values of $+2$ or -1 if the angular momentum is aligned in a plane parallel or perpendicular respectively to z .

If, however, the angular momentum quantum number, J , is small, the angular momentum distribution may no longer be treated classically as a continuous distribution about the z -axis and instead a quantum mechanical treatment of the angular momentum alignment and orientation is required. In this case, the spatial distribution of the angular momentum with rotational quantum number, J , is discussed in terms of its projection onto the z -axis, M_J , which may take any integer value in the range $-J$ to $+J$. For an isotropic distribution of angular momentum, the different M_J values will be equally populated and now orientation refers to a preference for a particular sign of M_J , whilst alignment refers to a preference for a particular magnitude of M_J .

Unequal M_J populations are, however, not the only cause of angular momentum polarisation and phase differences between the different M_J sublevels will also cause polarisation of the angular momentum along axes perpendicular to the z -axis.¹⁴ The populations and phases of the different $|J, M_J\rangle$ and $|J, M'_J\rangle$ states may be completely described in terms of the density-matrix formalism.¹⁵ The polarisation parameters are related to the elements, $\rho_{M'_J M_J}$, of the density-matrix describing the ensemble of angular momentum by the relation,^{10,13}

$$\rho_{M'_J M_J} = \sum_{k,q} (-1)^{J+q-M'_J} \frac{(2k+1)[J(J+1)]^{k/2}}{c(k) \langle J || J^{(k)} || J \rangle} \begin{pmatrix} j & k & j \\ -M_J & q & M'_J \end{pmatrix} A_q^{(k)}, \quad (1.8)$$

where $c(k)$ is a normalisation constant given in Ref. 13, chosen so that the polarisation parameters in the low- J limit coincide with the definitions given previously for the high- J limit, and the term in brackets is a Wigner-3j coefficient.¹⁰ In the low- J limit the angular momentum must be described in terms of the spherical tensor angular momentum operator, $J_q^{(k)}$, instead of the classical spherical harmonics and the elements, $\langle J || J^{(k)} || J \rangle$, appearing in the denominator of equation (1.8)

are reduced matrix elements of this operator and are tabulated in Ref. 10. Here the density-matrix elements where $M_J = M'_J$ give the populations of the different $|J, M_J\rangle$ states, whilst the matrix elements with $M_J \neq M'_J$ describe the phase differences and interference effects arising between states with different M_J .

For a rapid dissociation, if $\mathbf{J}$ is polarised in the molecular-frame and $\boldsymbol{\mu}$ is aligned in the laboratory-frame through photon absorption then a laboratory-frame alignment of $\mathbf{J}$ will also be expected. Also, if both $\mathbf{J}$ and $\mathbf{v}$ are correlated to $\boldsymbol{\mu}$ then there must also be a correlation between these vectors. Dixon¹⁶ expanded the correlated distribution of $\mathbf{J}$ and $\mathbf{v}$ about $\boldsymbol{\mu}$ in terms of the classical bipolar harmonics in a manner analogous to the expansion over the modified spherical harmonics in equation (1.4). The semi-classical bipolar moments, $\beta_Q^K(k_1, k_2)$, arising from this expansion completely describe the correlated distribution of $\mathbf{J}$ and $\mathbf{v}$ and have been determined successfully in many studies to quantify the angular momentum polarisation and translational anisotropy of photofragments in the high- J limit, where $\mathbf{J}$ may be treated classically. The derivation and interpretation of these bipolar moments will be discussed in more detail in chapter 3, where high- J NO fragments resulting from the UV dissociation of NO₂ will be investigated.

For atomic photofragments, J is low and therefore a quantum mechanical treatment to describe the angular momentum polarisation is required. Siebbeles *et al.*¹⁷ presented the first quantum mechanical treatment of the laboratory-frame angular momentum distribution in terms of a set of dynamical functions. Picheyev *et al.*¹⁸ have shown how normalised linear combinations of these dynamical functions yield a family of laboratory-frame polarisation anisotropy parameters which fully parametrise the angular momentum polarisation. Throughout this thesis the molecular-frame polarisation parameter formalism introduced by Rakitzis and Zare¹⁹ will be used. In this formalism the angular momentum distribution is expanded in terms of the $A_q^{(k)}(J)$ polarisation parameters, as in equation (1.4), which are defined in the molecular-frame and only describe the photofragment angular momentum distribution for pure parallel or perpendicular transitions. In order to describe the an-

gular momentum polarisation resulting from mixed transitions, the parallel and perpendicular contributions to the photoexcitation need to be separated and this is achieved by defining a set of closely related molecular-frame alignment parameters, $a_q^{(k)}(p)$, where p denotes the symmetry of the transitions excited; parallel ($\parallel$), perpendicular ($\perp$) or mixed ($\parallel, \perp$). This decomposition of the photofragment angular momentum alignment into incoherent contributions from parallel and perpendicular transitions as well as the coherent interference between these two contributions has been successfully applied to the one-photon dissociation of molecules such as ICl,^{20,21} OCS^{22,23} and Cl₂.^{21,24,25} In this thesis it will be shown how these parameters may be used to describe the photofragment angular momentum alignment resulting from the dissociation of Cl₂ in chapter 4 and O₂ in chapter 5. The conversion between the polarisation parameters used in this work and the many other formalisms used to describe angular momentum polarisation has been tabulated elsewhere.^{26–29}

1.3 An introduction to REMPI-TOF

Experimental techniques for studying photodissociation dynamics generally require the photolysis of the target molecule using an intense, polarised laser source followed by the state-selective detection of specific nascent photofragments. There have been many techniques developed which have successfully managed to measure the correlated distribution of $\mathbf{v}$ and $\mathbf{J}$ for specific photofragments and detailed descriptions of many of these techniques may be found in Refs. 3,30–32. This thesis will employ the technique of resonance enhanced multiphoton ionisation (REMPI) in combination with time-of-flight mass spectroscopy (TOF-MS) and this technique is now outlined.

REMPI involves promoting an atom or molecule to an excited state from which it may subsequently be ionised. This ionisation process is resonantly enhanced and scanning the probe laser will yield a REMPI spectrum where the ion signal intensity will increase as the probe wavelength becomes resonant with different optical transitions. The versatility of REMPI arises from the fact that the excited resonant state may be accessed by the absorption multiple photons and in this thesis, REMPI

schemes where the excited state is accessed *via* both one and two photons will be used and are illustrated in figure 1.3. REMPI transitions are labelled using the

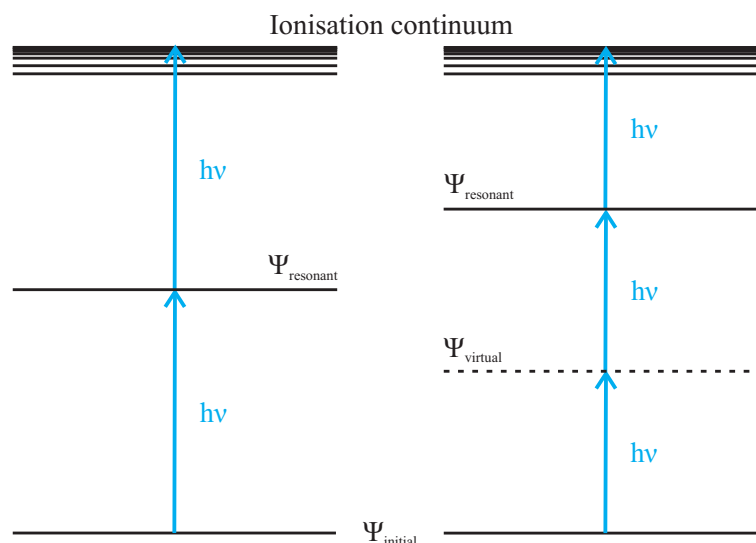


Figure 1.3: Illustrations of the energy levels involved in (1 + 1) (left) and (2 + 1) (right) REMPI schemes.

notation $(m + n)$, where m is the number of photons required to reach the resonant excited state and n is the number of photons required to ionise this state, and hence the transitions shown on the left and right of figure 1.3 are denoted (1+1) and (2+1) transitions respectively. The sequential absorption of two photons for the (2 + 1) transition occurs *via* a virtual intermediate state. This state may be considered as a coherent superposition of all possible real intermediate states and will be discussed further in chapter 5. The potential use of two or more photons to access a resonant excited state is a major advantage of REMPI since it allows excited states with very high energies to be probed using easily generated UV radiation, as opposed to the experimentally more challenging VUV radiation which would be required for a one photon transition. Additionally, two-photon excitations have different selection rules to one-photon excitations allowing excited states of different symmetries to be probed *via* allowed transitions. The selection rules for electric-dipole allowed one and two-photon transitions are summarised in table 1.1. The coherent absorption of

multiple photons requires intense light sources and therefore only with the advent of dye lasers has REMPI become a common technique for ion detection.³³

Table 1.1: Summary of the electric-dipole selection rules for one and two-photon absorption for atoms and Hund’s case (a) and (b) molecules, adapted from Ref. 33.

Property of interest	Number of photons	
	1	2
Atoms		
Orbital angular momentum of excited electron	$\Delta l = \pm 1$	$\Delta l = 0, \pm 2$ ($s \leftrightarrow s$)
Molecules		
Axial projection of electronic orbital angular momentum	$\Delta \Lambda = 0, \pm 1$	$\Delta \Lambda = 0, \pm 1, \pm 2$
Inversion symmetry (centrosymmetric molecules)	$u \leftrightarrow g$ $g \leftrightarrow u$	$g \leftrightarrow g$ $u \leftrightarrow u$
Atoms and molecules		
Total angular momentum	$\Delta J = 0, \pm 1$ $J = 0 \leftrightarrow J = 0$	$\Delta J = 0, \pm 1, \pm 2$ $J = 0 \leftrightarrow J = 0, 1$
Total parity	$+$ $\leftrightarrow$ $-$	$+$ $\leftrightarrow$ $+$
Electron spin	$\Delta S = 0$	$\Delta S = 0$

Once ions have been generated they are accelerated along a TOF mass spectrometer under the influence of electric fields onto a detector which measures the temporal distribution of ion arrival times, with the high sensitivity of the REMPI-TOF technique being due to the fact that a large fraction of the ions generated by each probe laser REMPI pulse will be detected. The ion arrival time will principally depend on the mass of the ionised fragment and this mass selectivity ensures that the identity of the detected photofragment is not in question, which may be a problem with alternative techniques like laser induced fluorescence (LIF) or Doppler spectroscopy if the different photofragments have overlapping transitions.³⁰ This mass selectivity also allows the determination of the angular momentum polarisation of isotopically different fragments, for example Cl^{35} and Cl^{37} discussed in chapter 4, which may have different angular momentum distributions.

In addition to its mass, the ion’s arrival time will also depend on the initial veloc-

ity of the ionised photofragments. The temporal width of a TOF profile allows the determination of the kinetic energy release of the probed photofragment which, by considering the conservation of energy, may be used to identify the specific dissociation channel. More subtly, the distribution of arrival times within this profile may be used to determine the translational anisotropy and angular momentum polarisation of the photofragments. Whilst there have been many advances to the standard TOF technique which have allowed 2D and 3D images of the initial photofragment distribution to be imaged directly,³² the 1D velocity projection obtained from the standard REMPI-TOF technique used in this thesis still allows a significant amount of information to be obtained on the dissociation dynamics of small molecules.

1.4 Summary

A brief introduction to the field of photodissociation dynamics has been presented. The experiments described in this thesis will aim to gain an insight into the fundamental forces involved in the dissociation process primarily through the measurement of correlated distributions of $\mathbf{v}$ and $\mathbf{J}$ for specific photofragments. A brief overview of the REMPI-TOF technique used throughout this thesis to measure these correlations has been presented and the next chapter will give a more detailed description of the experimental setup along with a detailed description of the theory required to model the observed TOF profiles. Chapter 3 will demonstrate how TOF profiles may be used to determine the correlated distribution of $\mathbf{v}$ and $\mathbf{J}$ in terms of the semi-classical bipolar moments for the high- J NO photofragments produced following the photodissociation of NO₂ at 320 nm. In chapter 4, attention will turn to measuring the photofragment angular momentum polarisation of the Cl atoms produced from the dissociation of Cl₂, which will be described in terms of the molecular-frame polarisation parameters, $a_q^{(k)}(p)$. Finally, in chapter 5 it will be shown how this polarisation parameter formalism may be extended to describe the angular momentum polarisation of O atoms following a two-photon predissociation of O₂.

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Chapter 2

Experimental

This chapter describes the experimental setup used for the majority of experiments described in this thesis. Most of the experiments employed two laser beams, which were used to generate and then ionise photofragments which were analysed using a modified Wiley-McLaren mass spectrometer. Firstly, a general description of the experimental setup is given which is followed by a more detailed description of the individual experimental components.

2.1 Experimental setup

A general overview of the experimental setup is shown in figure 2.1. Two counter-propagating laser beams were overlapped and aligned through the centre of the source region of a modified Wiley-McLaren mass spectrometer. An effusive molecular beam of the target molecule was generated by a pulsed valve and is crossed at right angles by the two counter-propagating beams at the centre of the source region. The first laser beam photolyses the molecule of interest, whilst the second, probe laser beam state selectively ionises the nascent atomic or molecular photofragments. The resulting ions are accelerated under the influence of homogeneous electric fields down the drift tube of the Wiley-McLaren mass spectrometer. These ions are detected by a microchannel plate (MCP) detector and the temporal distribution of

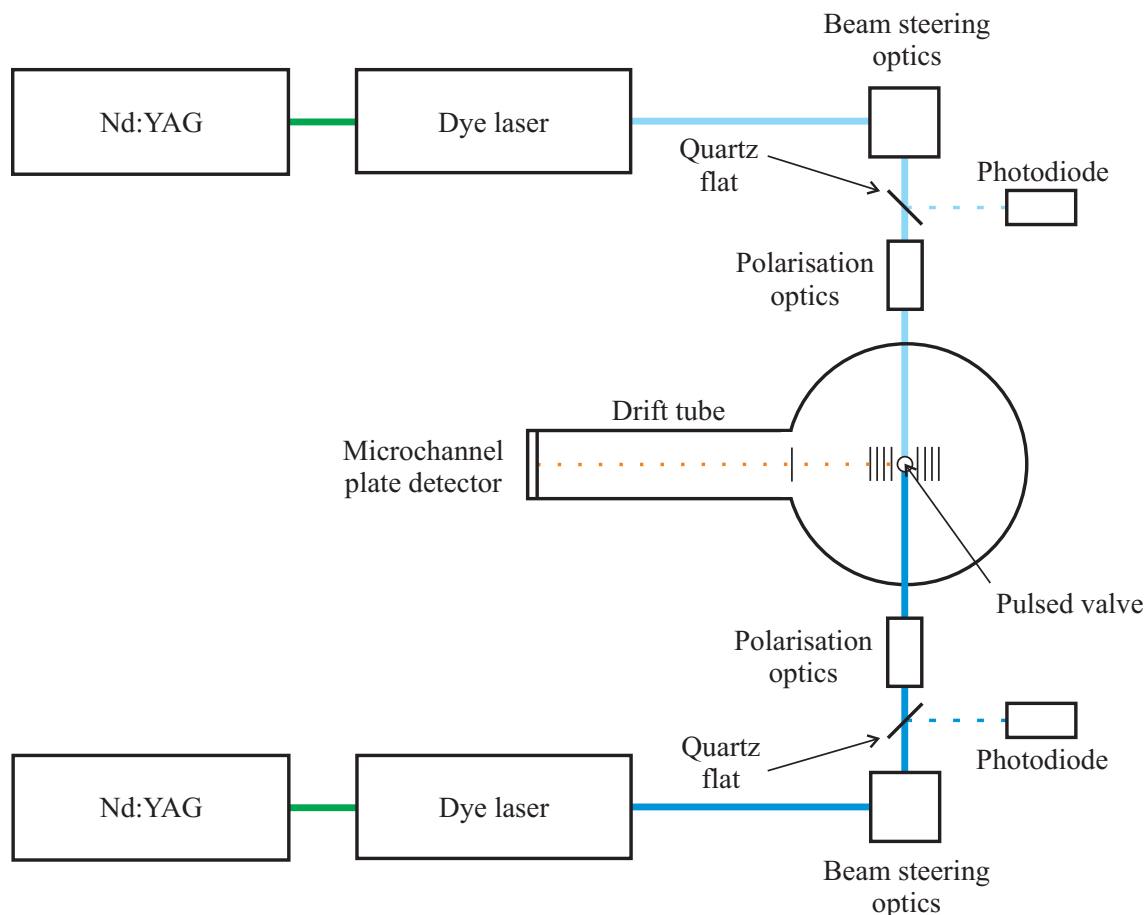


Figure 2.1: Schematic diagram illustrating the experimental setup used for the experiments carried out in this thesis.

arrival times is recorded on a digital oscilloscope.

2.1.1 Laser Systems

The laser beams used in this thesis were generated by two Nd:YAG pumped dye laser systems. The photolysis laser beam was generated using an LAS LDL 2051 dye laser pumped by a Spectra-Physics Nd:YAG laser. For this dye laser system the YAG laser was employed in Q-switching mode, whereby an optical switch in the laser cavity waits for maximum population gain to be achieved in the laser medium prior to opening, generating laser pulses with a short temporal width (~ 10 ns) and high output power. This laser output is produced at a fundamental frequency of

1064 nm which is doubled using a potassium dideuterium phosphate (KD*P) crystal to produce 532 nm radiation which is required to pump the resonator/preamplifier and main amplifier cells of the LAS LDL 2051 dye laser. The laser radiation used to ionise the NO, Cl and O(³P) photofragments studied in this thesis was generated using a Sirah CSTR-G-2400 dye laser pumped by a Continuum Surelite II-10 Nd:YAG laser. For this dye laser system the YAG laser was also employed in Q-switching mode, with the laser output tripled using two KD*P crystals to produce 355 nm radiation and used to pump the Sirah CSTR-G-2400 dye laser. For both these laser systems, the dye laser output was doubled by a β -barium borate (β -BBO) crystal to achieve the required UV wavelength, with a set of Pellin-Broca prisms used to separate the dye laser fundamental radiation from the desired frequency doubled radiation. The two generated photolysis and probe laser beams were subsequently overlapped and aligned through the centre of the main chamber of the Wiley-McLaren mass spectrometer *via* a set of prisms.

To generate the radiation required to probe O(¹D₂) photofragments, the frequency tripled output of the Sirah CSTR-G-2400 dye laser pumped by a Continuum Surelite II-10 Nd:YAG laser was used. For this system the YAG laser was frequency doubled using a KD*P crystal to produce 532 nm radiation, which was subsequently used to pump the Sirah CSTR-G-2400 dye laser. The output of the dye laser was doubled using a β -BBO crystal and the polarisations of the doubled and fundamental laser beams were matched using a dual-wavelength waveplate which only rotated the doubled laser polarisation (Sirah RP-080). These two laser beams were subsequently passed through a second β -BBO crystal to produce the required wavelength *via* sum frequency generation.¹ This frequency tripled radiation was separated from the dye fundamental and doubled radiation using a set of four dichroic mirrors and aligned using a further set of high reflectivity mirrors. A summary of the laser dyes used throughout this thesis is given in table 2.1, where all dyes were dissolved in spectroscopic grade ethanol or methanol.

In order to ensure that all photofragment velocity groups were detected equally,

experiments were performed by stepping the wavelength of the probe laser over the entire Doppler width of the probe transition. This ensures that there was no problem of Doppler selection and no photofragment velocities were preferentially detected.

Table 2.1: Summary of the laser dyes used to generate the wavelength regions required throughout this thesis.

Nd:YAG pump frequency / nm	Laser dye	Fundamental wavelength / nm	Solvent
532	Pyridine 1	645 – 730	Ethanol
532	DCM	610 – 660	Methanol
532	Rhodamine 640/610	594 – 629	Methanol
532	Rhodamine 610	576 – 600	Methanol
355	Coumarin 480	460 – 500	Ethanol
355	Coumarin 450	436 – 467	Ethanol

2.1.2 Polarisation control

Accurate determinations of the vector correlations measured in this thesis require TOF profiles to be recorded in a series of geometries where the photolysis and probe laser polarisations are well defined. Generally, angular momentum alignment and translational anisotropy parameters were determined by fitting simulations to the sum and difference of complimentary pairs of experimental geometries. The exact geometries used will be described in the next section, however, all pairs of geometries require one laser beam to be set at a fixed linear polarisation, whilst the other, counter-propagating laser beam is switched between horizontal and vertical polarisation or left and right circular polarisation. The fixed linear polarisation was achieved by using a $\lambda/2$ -waveplate (Thorlabs) followed by a α -BBO Glan-Taylor polariser (Casix). Rotation of the laser beam using the $\lambda/2$ -waveplate before the polariser also allowed control of the power of the laser used in the experiments.

The switched polarisation was achieved using a photoelastic modulator (Hinds Instruments Inc., PEM-90). The PEM's operation is based on the photoelastic effect, whereby a mechanically stressed sample exhibits birefringence proportional to

the resulting strain.² Specifically, a fused silica bar is attached to a piezoelectric transducer which forces it to vibrate along its longest dimension at a natural resonance frequency of 50 Hz. This causes an oscillating birefringence to occur at the centre of the bar *via* the photoelastic effect. The initial laser beam is horizontally polarised using a $\lambda/2$ -waveplate followed by a α -BBO Glan-Taylor polariser as described earlier. It is then aligned through the centre of the PEM, which is orientated so that the modulator axis is at 45° to the horizontally polarised laser beam. If the fused silica bar is relaxed when the laser beam passes through the PEM then the polarisation will be unchanged and horizontally polarised light is transmitted. If, however, the fused silica bar is stressed when the laser beam passes through, the birefringence resulting from the photoelastic effect will cause the electric field component of the laser beam that is parallel to the modulator axis to travel faster than the perpendicular component. Conversely, if the silica bar is stretched the perpendicular component will travel faster. This results in a phase difference between the two components called the retardation which will vary sinusoidally as the bar vibrates. The PEM may be set so that at peak retardation this phase difference is $\pm\lambda/2$, resulting in vertically polarised light, or $\pm\lambda/4$, resulting in right or left circularly polarised light.² The Q-switch of the laser was carefully timed so that each shot passed through the PEM at a specific point in the PEM's retardation cycle to produce the required polarisation for the specific experimental geometry. This has the advantage that both complimentary geometries may be recorded in a single experimental run, ensuring that they are recorded under identical conditions.

For experiments where the PEM was used to switch between linear polarisations a Glan-Taylor polariser placed after the PEM was used to calibrate the exact delays required to produce the desired polarisations. For experiments where circular polarised light was employed the method described by Alexander³ was used to determine the absolute helicity of the light. This consisted of placing a Fresnel-Rhomb after the PEM, which generates light linearly polarised at $\pm 45^\circ$ to the vertical plane depending on whether the light is left or right circular polarised, with a Glan-Taylor

polariser placed after the Fresnel-Rhomb to determine the angle of this linear polarised light and therefore the helicity of circular polarised light produced by the PEM at a specific time delay.

2.1.3 Experimental timing

The flash lamps of the YAG lasers were fired and following a delay of approximately $185 \mu\text{s}$ the Q-switches were triggered producing the maximum power laser pulse. The photolysis laser's Q-switch was triggered at an optimised time delay of 1.25 ms after the pulsed valve so that each laser shot intersected the maximum density within the pulsed molecular beam. This time delay was determined *via* a one-laser experiment where the total REMPI signal detected for a sample of NO was recorded as a function of the time delay between the REMPI laser and the pulsed valve and is shown in figure 2.2.

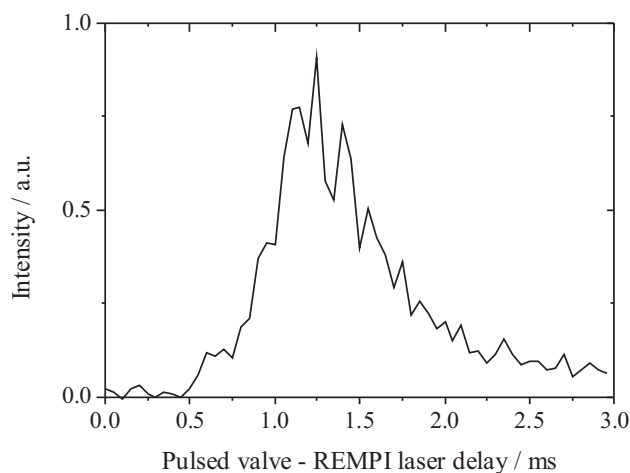


Figure 2.2: Total REMPI signal measured as a function of the delay between the REMPI laser and the pulsed valve.

The Q-switch of the second, probe laser was fired at a variable time delay of approximately $\sim 25 \text{ ns}$ after the photolysis laser. The pulsed valve was triggered so that the photolysis or probe laser shot coincided with the specific point in the

PEM's retardation cycle to produce the required polarisation. These timings were controlled by a pulse generator (Quantum Composers 9582, 250 ps resolution, 50 ps jitter) under computer control *via* a RS232 interface.

A partial reflection of both laser beams was generated using a quartz flat and was detected by two independent fast photodiodes (Lambda Physik LF 302 UV) which were monitored on a digital storage oscilloscope (LeCroy 9350A, 500 MHz 10^{-9} samples s^{-1}). This allowed the the delay time between the two laser beams to be monitored and for the detected TOF profiles to be power normalised for shot-to-shot variations in the laser power. The temporal distribution of arrival times of the ions is recorded on a second digital storage oscilloscope (LeCroy 9350, 1 GHz, 10^{-9} samples s^{-1}). Both oscilloscopes are triggered by a fast photodiode which detects the probe dye laser pulse (Hamamatsu S1722-02, 1 ns rise time, spectral range 190 – 1060 nm).

Experiments were generally performed with four different time delays in the same experimental run. There were two time delays corresponding to switching the polarisation of one of the lasers *via* the PEM in order to record both complimentary experimental geometries. In many of the experiments in this thesis, the probe laser on its own produced a significant one-laser signal. In order to account for this, measurements were also taken with the photolysis laser triggered a long time after the probe laser to record the probe only signal. These were subsequently subtracted from the measured two-laser signal for both geometries, following power normalisation, to yield the true pump-probe signal resulting from both lasers. TOF profiles measured in these four time delays, corresponding to two experimental geometries and their backgrounds, were recorded and averaged over 100 laser shots on a digital oscilloscope before stepping the wavelength of the probe laser. Typically, TOF profiles were averaged over a total of 3000 shots once the entire Doppler profile of the the probe transition had been scanned over, which was found to produce a sufficient signal-to-noise ratio.

2.2 Time-of-flight mass spectrometer

2.2.1 Experimental details

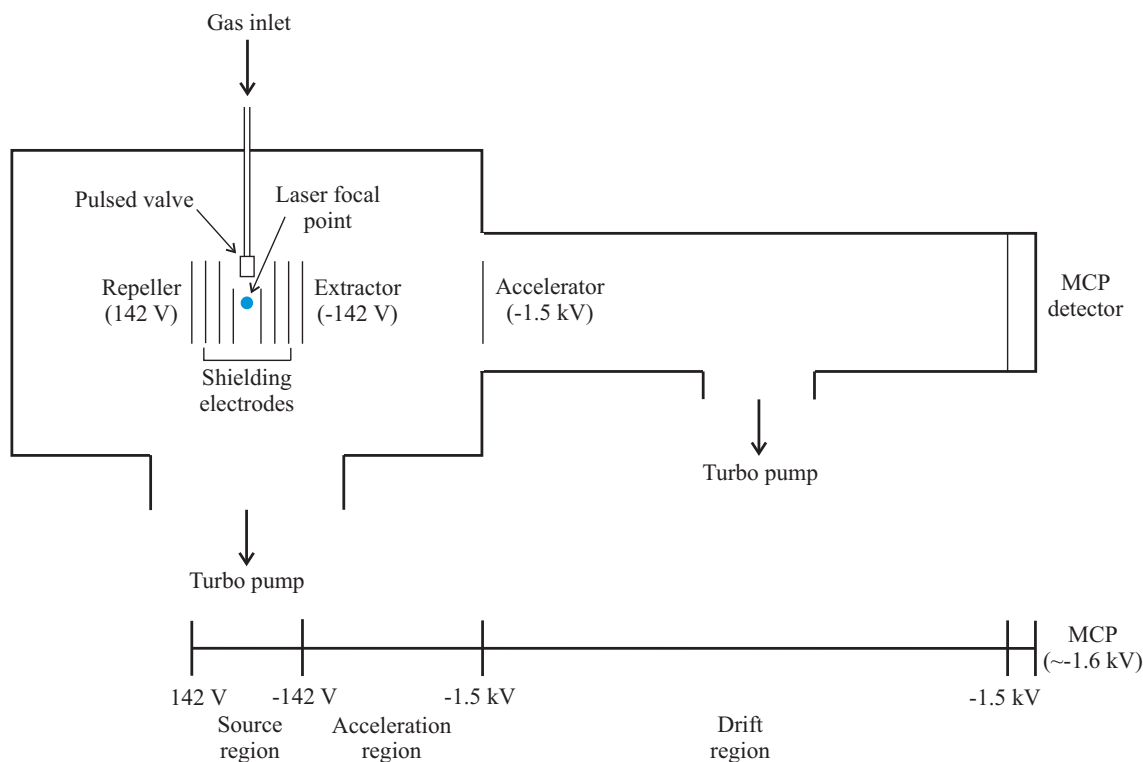


Figure 2.3: Schematic diagram illustrating the setup of the time-of-flight mass spectrometer used for the experiments carried out in this thesis.

The ions generated by the REMPI laser pulse were analysed using a TOF mass spectrometer, the basic design of which was first proposed by Wiley and McLaren in 1955,⁴ and a schematic diagram of this is shown in figure 2.3. This spectrometer consists of two main sections, the main chamber and the drift tube. To ensure measurement of nascent velocity distributions, the operating pressures within the spectrometer are kept sufficiently low to ensure that no collisions affect the flight path of the ions. Additionally, the MCP detector requires the pressure in the drift tube to be maintained below 2×10^{-6} Torr. These high vacuum conditions were achieved in the main chamber using a turbo-molecular pump (Leybold TMP 600C)

backed by a rotary pump (Leybold D40B). At the centre of the main chamber an effusive molecular beam was generated using a pulsed solenoid valve (Parker series 9, nozzle diameter 152 μm). The backing pressure of gas used in the pulsed valve was typically 300 Torr, monitored by a capacitance manometer (Diametrics Baratron, 1 – 100 Torr), of a mixture of 20% of the target molecule in helium. This molecular beam was directed at the turbo-molecular pump and a purge of nitrogen was used to prevent corrosive reagent gases, especially Cl_2 , from corroding the bearings of the pump. The drift tube was pumped by a further, smaller turbo-molecular pump (Leybold 361C) backed by a rotary pump (Leybold D40B). The pressure in both the main chamber and the drift tube was monitored using Bayard-Alpert type ion guage tubes (Varian 563 or Duniway I-100-K). With the pulsed valve off, typical pressures were 5×10^{-8} and 1×10^{-7} Torr in the main chamber and drift tube respectively. With the pulsed valve on, the amplitude of the valve opening was controlled so that the pressure in the main chamber was maintained at 5×10^{-6} Torr, whilst the pressure in the drift tube was 10^{-6} Torr, with the mean free path of molecules at these pressures sufficiently large enough to ensure that only nascent photofragments are detected by the spectrometer. The pressure in the main chamber was monitored continuously during experiments, whilst ions produced by the ion guage on the drift tube caused unwanted background signals so this guage was turned off during experimental runs. Frequent checks were made to ensure that the shapes of experimentally measured TOF profiles were unaffected by an increase in operating pressure and therefore confirming that the measured ion distribution was truly nascent.

The two counter-propagating photolysis and probe laser beams were focused at the centre of the main chamber using two 250 mm focal length lenses mounted on translation stages to facilitate maximum overlapping of the two focal points. The pulsed valve was positioned 17 mm above the overlapped focal points of the two lasers. The Mach disc for a molecular beam operating under the conditions described in this section is calculated to be 2.6 m and therefore the section probed by the lasers is well within the supersonic expansion region of the molecular beam.⁵

The photofragment ions produced by the photolysis and probe laser beams are subsequently accelerated along the TOF axis towards the detector under the influence of homogeneous electric fields. The acceleration of the ions occurs in two stages. The first is the source region, which has the focal point of the two laser beams at its centre, where extractor and repeller plates produce a relatively weak electric field which steers the initially formed ions towards the detector. The close proximity of the pulsed valve to the centre of the source region was necessary to ensure that a high density of molecules were probed, however, the pulsed valve is necessarily grounded and could therefore cause a distortion of the homogeneous electric field in the source region. This effect was avoided by a series of equally spaced shielding electrodes placed either side of the pulsed valve linked by a resistor chain to the extractor and repeller plates. The second region is the acceleration region where a much stronger electric field is used to rapidly accelerate the ions towards the detector. After the acceleration region, ions enter a drift region held at a constant voltage with a MCP detector at the end. Ions travelling along the drift region could be steered onto the detector using two pairs of steering plates which could be set to produce small electric fields perpendicular to the TOF axis. Wire mesh grids were used to separate the regions with different electric field strengths to ensure that all fields remained homogeneous and undistorted by neighbouring fields.

The MCP detector in fact consists of two MCPs (Galileo 1397-1816, 18 mm active diameter). Ions impacting on the first plate release an electron which travels through the channels of both plates releasing further electrons. This avalanche of electrons is subsequently accelerated from the back face of the second plate, held at -200 V, towards a grounded output. The gain of the detector is determined by the potential difference between the front face of the first plate and the back face of the second. For the experiments carried out in this thesis the front face of the first plate was generally held at potentials between -1.55 and -1.65 kV depending on the signal levels of the particular experiment. This potential difference of $1.35 - 1.45$ kV across the two MCP plates results in a gain in the region of 10^6 electrons per ion

impact. The output signal from the MCP detector is further amplified by a fast pulse amplifier (Mini Circuits ZPUL-30P) and averaged over 100 laser shots on an oscilloscope before being stored on a PC.

2.2.2 Simulating the time-of-flight profile

An ion with a charge, q , and mass, m , situated between two electrodes with a potential difference, ΔV , will experience a force which results in an acceleration, a , of the ion given by,

$$a = -\frac{q}{m} \left(\frac{\Delta V}{s} \right), \quad (2.1)$$

where s is the distance between the two electrodes. Using simple equations of motion, an ion's final velocity, v_f , after travelling a distance, d , in this uniform electric field can be calculated to be,

$$v_f = \sqrt{v_i^2 + 2ad}, \quad (2.2)$$

where v_i is the initial velocity of the ion. The time-of-flight, t , for an ion to travel a distance, d , in a homogeneous electric field is therefore given by,

$$t = \frac{2d}{v_i + v_f}. \quad (2.3)$$

The total flight time, t_{total} , for an ion travelling under the influence of the electric fields in the spectrometer is given by the sum of the flight times for each of the four regions of homogeneous electric fields,

$$t_{total} = t_{source} + t_{acceleration} + t_{drift} + t_{MCP}. \quad (2.4)$$

The initial velocity for each region is given by the final velocity of ion travelling through the preceeding region, apart from the source region where the flight time is determined by the ion's initial velocity along the TOF axis at the instant of generation by the REMPI laser pulse. This ability to resolve the ion's initial nascent

velocity distribution is the most important aspect of the experimental setup for the work described in this thesis.

Table 2.2: The potential difference and electrode separation for each of the four regions of homogeneous electric fields in the TOF spectrometer.

Region	Potential difference / V	Electrode separation / m
Source	284	0.035
Acceleration	1358	0.028
Drift	0	0.860
MCP	50 – 150	0.016

The potential difference and electrode separation used for each of the regions of the TOF spectrometer used in the work described in this thesis are given in table 2.2. Note that the distance travelled by the ion in the source region is half the electrode separation since the pulsed valve is positioned in the middle of the repeller and extractor plates. Using these dimensions an ion's flight time, which will depend on its mass, charge and initial velocity along the TOF axis, can be calculated. A flight time, t_0 , for an ion formed with no initial velocity along the TOF axis can therefore be calculated which, for example, for an NO^+ ion is $10.47 \mu\text{s}$. If an ion has a non-zero initial velocity then the flight time of the ion will be slightly different. This correction to the flight time due to the ion's initial velocity, t' , is call the TOF shift and is given by,

$$t' = \frac{mv_{\text{source},i}}{qE_{\text{source}}}, \quad (2.5)$$

where $v_{\text{source},i}$ is the component of the ion's initial velocity along the TOF axis in the source region and E_{source} is the electric field strength of the source region. The measured TOF profiles will therefore be centred around the time, t_0 , for each specific ion mass with a range of flight times either side due to this TOF shift. The kinetic energy of the ionised photofragments, KE_{ion} , can be simply calculated by considering

both conservation of momentum and energy so that,

$$KE_{\text{ion}} = \left(\frac{m_{\text{co}}}{m_{\text{ion}} + m_{\text{co}}} \right) \left(\frac{hc}{\lambda} - E_{\text{diss}} + E_{\text{int}}(\text{molecule}) - E_{\text{int}}(\text{fragments}) \right), \quad (2.6)$$

where m_{ion} is the mass of the ion, m_{co} is the mass of its co-fragment, h is Planck's constant, c is the speed of light, λ is the wavelength of the photolysis laser, E_{diss} is the minimum energy required to photolyse the parent molecule, $E_{\text{int}}(\text{parent})$ is the internal energy of the parent molecule prior to dissociation and $E_{\text{int}}(\text{fragments})$ is the internal energy of both photofragments formed following dissociation. From this kinetic energy the magnitude of the velocity of the ion with the maximum TOF shift, t'_{max} , occuring when this velocity is directed entirely along the TOF axis either directly towards or away from the detector can be calculated. For an isotropic sample of ions of a specific mass, the measured TOF profile will therefore have a “top hat” shape as shown in figure 2.4 where the width of the profile is defined by t'_{max} .

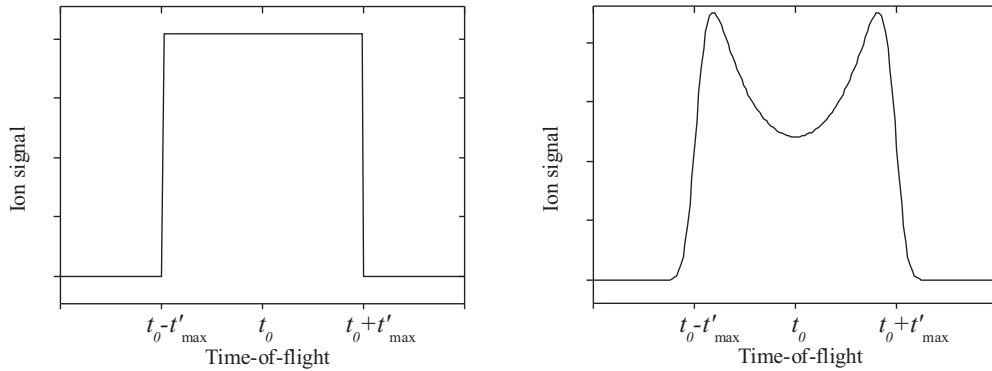


Figure 2.4: Simulations of TOF profiles detecting an ensemble of ions with an isotropic initial velocity distribution in the absence of any experimental effects (left) and after accounting for core extraction and the temporal width of the probe laser pulse (right). The values of the parameters used to simulate the core extraction and the temporal width were $\sigma = 10$ ns, $C_1 = 1$ and $C_2 = 1.1$.

As mentioned previously, the main aim of the experiments carried out in this thesis is to determine the nascent velocity distribution of the photofragments and

therefore this TOF shift should be made as large as possible to obtain the best possible resolution of this velocity distribution. As can be seen from equation (2.5), the magnitude of the TOF shift is determined by the electric field strength of the source region and therefore by setting the potential difference in this region to be as low as possible the best resolution is obtained. However, if ions aren't accelerated fast enough along the TOF axis a problem occurs whereby ions formed with sufficient velocity perpendicular to the TOF axis will simply miss the MCP detector. The main advantage of the two step acceleration employed in the spectrometer used in this work is that it allows the potential difference in the source region to be set relatively low to achieve high resolution TOF profiles whilst the much higher potential difference in the acceleration region ensures that ions are accelerated fast enough so that the majority will reach the detector.

Another advantage of the two step acceleration is that it is possible to account for ions being formed at slightly different positions in the source region due to the finite size of the focal point of the REMPI laser. This is achieved by setting the potential of the repeller, extractor and accelerator plates in a specific ratio so that *space focussing* conditions are met. Space focussing relies on the fact ions formed further from the extractor plate will experience a slightly larger acceleration in the source region and will therefore catch up ions formed closer to the detector. It is therefore possible to calculate the electrode voltages required so that ions formed at slightly different distances from the detector will arrive at the same time. It has been calculated that repeller, extractor and accelerator plate voltages in the ratio $1 : -1 : -10.56$ fulfill this condition⁶ and therefore the repeller, extractor and accelerator voltages of 142, -142 and -1500 V used in this work achieve space focussing.

Measured TOF profiles of ions formed with an isotropic velocity distribution will, in fact, not look exactly like the “top hat” profile shown in figure 2.4 due to experimental factors affecting the measured profile. As mentioned earlier, ions formed with a sufficiently large velocity component perpendicular to the TOF axis will miss

the detector. The voltages employed in the spectrometer represent a compromise between resolution of the TOF shift and ensuring ions reach the detector and whilst the majority of ions will reach the detector some will miss. This effect is termed *core extraction* and whilst it is an experimental problem in our experiments it has been achieved deliberately in other studies.⁷ In those studies a skimmer is used to only allow ions travelling parallel to the TOF axis to reach the detector resulting in increased resolution of ions formed with slightly different kinetic energies. For example, Rakitzis *et al.*⁸ have used this technique to resolve Cl atoms formed by the photolysis of Cl₂ in both its ground and vibrationally excited states. For the experiments described in this thesis, however, this increased resolution is not necessary and therefore a core extractor was not used. Core extraction is accounted for in the simulations of profiles used in this thesis by defining two parameters C_1 and C_2 .⁹ The first parameter, C_1 , defines the ratio of perpendicular to parallel velocity components along the TOF axis, $\frac{v_{\perp}}{v_{\parallel}}$, below which the ion will definitely hit the detector whilst the second parameter, C_2 , defines the ratio above which it will definitely miss the detector. At velocity ratios between C_1 and C_2 the probability that an ion will hit the detector must lie between 0 and 1 due to imperfections at the edge of the MCPs and ions being formed at slightly different positions in the source region. This probability is modelled as decreasing linearly from 1 to 0 as the velocity ratio increases from C_1 to C_2 . Core extraction has the effect of producing a dip at the centre of the TOF profile since these ions are most likely to miss the detector.

The second experimental factor which should be accounted for is the finite temporal width of the REMPI laser pulse. This is approximately ~ 10 ns for the YAG pumped dye lasers used in this thesis and results in a slight smearing of the overall observed TOF profile. This is accounted for by convoluting the simulated TOF profiles with a Gaussian function which has a full width half maximum (FWHM) given by,⁹

$$\text{FWHM} = \frac{\sigma}{\sqrt{n}}, \quad (2.7)$$

where σ is the FWHM of the probe laser pulse and n is the REMPI power dependence of the total ion signal, which is determined experimentally. In figure 2.4 is a simulated TOF profile, which has been corrected for both core extraction and the temporal width of the probe laser using typical values for the parameters σ , C_1 and C_2 , shown alongside the ideal “top hat” profile. In practice, the exact values of these parameters are determined experimentally and will be discussed further in the next chapter.

Finally, if the bandwidth of the probe laser is comparable to or smaller than the Doppler width of the REMPI transition then ions with specific velocities will be preferentially selected. This is termed *Doppler selection* and will result in an anisotropic velocity distribution of ionised photofragments. As discussed earlier, this is accounted for in our experiments by stepping the probe laser wavelength over the entire REMPI transition, thus ensuring that all photofragment velocities are detected equally. Once all of these experimental factors have been accounted for, any further deviations of the measured TOF profile from the simulated TOF profile must result from an initially anisotropic ion velocity distribution. An anisotropic ion velocity distribution may result from either a translational anisotropy of the photofragments produced by the photolysis laser pulse or an anisotropic ionisation probability of these photofragments by the probe laser due to angular momentum alignment. The next chapter will show how this anisotropy may be modelled and used to extract information on the dynamics of the dissociation process.

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Chapter 3

The photodissociation of NO₂ at 320 nm

This chapter describes measurements of photofragment angular momentum orientation and alignment following the dissociation of NO₂ at 320 nm. The angular momentum polarisation is described in terms of bipolar moments and this chapter demonstrates how these parameters may be extracted from TOF profiles taken in a series of different geometries. The rotational temperature of the parent NO₂ molecules is found to have a significant effect on the measured angular momentum polarisation of the NO photofragments and these effects have been quantified.

3.1 Introduction

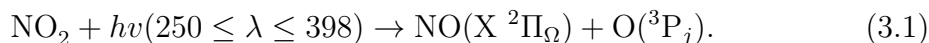
The UV photodissociation of NO₂ has been widely investigated over many years.¹ This is partly due to its important role within the chemistry of the atmosphere where it is intimately linked with ozone chemistry in both the stratosphere and the troposphere. In the stratosphere, the key role of NO₂ photolysis is within *null cycles* in which NO₂ and NO inter-convert leading to net depletion of the ozone layer without the loss of odd-oxygen, whilst in the troposphere NO₂ photolysis contributes to the only true tropospheric source of ozone production.² More significantly for this work, however, the open-shell electronic structure of NO₂ gives rise to highly coupled electronic states and complex dissociation dynamics, which have resulted in the photodissociation of NO₂ becoming a key benchmark in the study of fundamental

dissociation dynamics.¹

The valence configuration of NO₂ consists of 17 electrons that result in a ground electronic state with a bent nuclear configuration and doublet spin multiplicity. The electronic configurations are labeled in terms of C_{2v} symmetry and the ground electronic state, X ²A₁, has an electronic configuration of (4b₂)²(6a₁)¹ for the two highest energy occupied valence molecular orbitals.^{3,4} The stability of these valence molecular orbitals is very sensitive to the O-N-O bond angle with the 6a₁ molecular orbital, containing the unpaired electron, being antibonding and stabilised by reducing the bond angle and the 4b₂, which is doubly occupied, being stabilised by increasing the bond angle. A balance of these two effects results in an equilibrium bond length for the ground electronic state of 134.25°.⁵

The first electronic absorption band, in the wavelength region (250 – 667) nm, consists primarily of excitation to the ²B₂ electronic state with a very small contribution from excitation to the ²B₁ state. Excitation to the ²B₂ state is due to a 6a₁ ← 4b₂ transition and therefore, due to the preference of the 6a₁ molecular orbital for a reduced bond angle, the equilibrium bond angle of the ²B₂ state is reduced from that of the ground state to 111°.⁵ The ²B₂ state is effectively mixed with the ground X ²A₁ state due to a conical intersection between the two PESs near the ²B₂ minimum. This mixing is promoted by the antisymmetric stretching mode of the NO₂ molecule and occurs at bond lengths close to 126 pm and bond angles close to 108°.^{6,7}

The threshold wavelength for dissociation is at 398 nm ($\sim 25,000 \text{ cm}^{-1}$)⁵ and absorption of photons above the threshold energy results in the photolysis of NO₂ studied in this chapter. Absorption of photons in the wavelength region (250 – 398) nm results in the production of ground state, X ²Π_Ω, NO molecules and O(³P_{*j*}) atoms,



This dissociation is due to a rapid predissociation of the ²B₂ state facilitated by the conical intersection described previously. Upon absorption of a photon to excite the

²B₂ state, the NO₂ bond angle is reduced as the nuclear framework relaxes towards the equilibrium geometry of the ²B₂ state enabling ultra-fast internal conversion to occur to the X ²A₁ state; the nuclear configuration of the conical intersection is accessed within 10 fs of excitation^{6,7} and asymmetric stretch motion then results in a barrierless dissociation along the ground state.

There have been many studies focussing on the NO rotational state distributions and these have provided an excellent test of statistical theories describing dissociation process. Close to the dissociation threshold the transition state is found to be very loose and the rotational distributions are found to be well described on average by phase space theory (PST).^{8,9} Here excited state lifetimes are relatively long (~ 50 ps)^{10–12} and the decomposition rate is limited by the timescale of the intramolecular vibrational redistribution required for fragmentation. As the excess energy increases the transition state is found to tighten and the excited state lifetime decreases resulting in increasingly non-statistical rotational distributions. At energies much higher than the dissociation threshold the excited state lifetime reduces to less than 100 fs^{10–13} and rotational distributions are found to be bimodal.¹⁴

Whilst these studies of the scalar properties of the dissociation process have clearly provided a great deal of insight into the complicated dissociation mechanism, this chapter will concentrate on the complimentary information which may be obtained from measurements of the spatial properties of the dissociation process. This is achieved by considering the correlations existing between the three vectors of interest during a photodissociation process; the velocity, $\mathbf{v}$, and rotation, $\mathbf{J}$, of the detected photofragments and the transition dipole, $\boldsymbol{\mu}$, of the parent molecule. There have been many previous studies of these vector correlations for the absorption band studied in this chapter and these studies will be discussed later and compared to the results presented in this work.

3.2 Determining vector correlations

This section will demonstrate how the correlations between the vectors $\mathbf{v}$, $\mathbf{J}$ and $\boldsymbol{\mu}$ may be described in terms of a semiclassical bipolar moment formalism developed by Dixon,¹⁵ how these vector correlations affect the final measured TOF profiles and hence how they may be extracted from profiles taken in a series of experimental geometries.

3.2.1 Relating TOF profile to bipolar moments

The description of the correlations between $\mathbf{v}$, $\mathbf{J}$ and $\boldsymbol{\mu}$ in terms of bipolar moments and how this affects the measured TOF profile has been performed explicitly by Dixon for LIF measurements¹⁵ and first modified for REMPI-TOF detection by Mons and Dimicoli.¹⁶ In this section the approach of Uberta *et al.*¹⁷ will be used and a brief overview of the steps required to relate these bipolar moments to the measured TOF profiles will be given. In the high- J limit, the correlated spatial distribution of $\mathbf{v}$ and $\mathbf{J}$ of the detected photofragment may be expanded in terms of the classical bipolar harmonics, B_{KQ} , of rank K and component Q , which are given by,^{15,18}

$$B_{KQ}(k_1 k_2; \theta_t \phi_t \theta_r \phi_r) = \sum_{q_1} \sum_{q_2} (-1)^{K-Q} [K]^{1/2} \begin{pmatrix} k_1 & K & k_2 \\ q_1 & -Q & q_2 \end{pmatrix} C_{q_1}^{k_1}(\omega_t) C_{q_2}^{k_2}(\omega_r), \quad (3.2)$$

where $[X] \equiv (2X + 1)$ and $C_q^k(\omega)$ are modified spherical harmonics.¹⁸ $\omega_t \equiv (\theta_t, \phi_t)$ and $\omega_r \equiv (\theta_r, \phi_r)$ are the polar angles describing $\mathbf{v}$ and $\mathbf{J}$ relative to the reference z -axis. The allowed ranges of the different ranks and components of the bipolar harmonic will depend on the details of the dissociation and probe process and will be discussed later. These bipolar harmonics are defined in a *body-fixed* reference frame where the z -axis is given by the transition dipole, $\boldsymbol{\mu}$, of the parent molecule at the instant of absorption of a dissociation photon. These bipolar harmonics provide a complete set of functions in the space spanned by the two directions, ω_t

and ω_r , relative to $\boldsymbol{\mu}$. The classical, correlated angular probability density function for the spatial distribution of $\mathbf{v}$ and $\mathbf{J}$ defined in the body-fixed reference frame, $P(\mathbf{v}, \mathbf{J})$, can therefore be expanded in terms of these bipolar harmonics to give,¹⁵

$$P(\mathbf{v}, \mathbf{J}) = \sum_K \sum_Q \sum_{k_1} \sum_{k_2} \frac{[k_1][k_2]}{16\pi^2} b_Q^K(k_1 k_2) B_{KQ}(k_1 k_2; \omega_t \omega_r), \quad (3.3)$$

where the coefficients of this expansion, $b_Q^K(k_1 k_2)$, are the bipolar moments and are expectation values of the bipolar harmonics given by,

$$b_Q^K(k_1 k_2) = \int B_{KQ}(k_1 k_2; \omega_t \omega_r)^* P(\omega_t, \omega_r) \sin \theta_t \sin \theta_r d\theta_t d\phi_t d\theta_r d\phi_r. \quad (3.4)$$

These bipolar moments form a complete set of parameters which completely describe the spatial distribution of the $\mathbf{v}$ and $\mathbf{J}$ vectors of a specific photofragment with respect to the transition dipole of the parent molecule. These bipolar moments are subsequently renormalised so that they have more convenient limits and are denoted $\beta_Q^K(k_1 k_2)$.

This correlated angular probability density function is now transformed into the laboratory-fixed, *dissociation* reference frame where the z -axis is now parallel to the electric vector of the photolysis laser, $\boldsymbol{\epsilon}_{\text{phot}}$.¹⁵ The absorption probability of a one-photon electric-dipole allowed transition is given by $|\boldsymbol{\mu} \cdot \boldsymbol{\epsilon}_{\text{phot}}|^2$ and integration of the body-fixed $P(\mathbf{v}, \mathbf{J})$ over this probability distribution will transform it into the dissociation frame. The rotational moments, $\rho_q^k(J)$, of the angular distribution of $\mathbf{J}$ in the dissociation frame are found by projecting this distribution onto a basis of modified spherical harmonics, $C_q^k(\theta_r, \phi_r)$. The $\mathbf{v}$ -dependence of these rotational moments is now rotated into the *detector* frame *via* an Euler rotation of $(0, \theta_D, 0)$, where θ_D is the angle between $\boldsymbol{\epsilon}_{\text{phot}}$ and the TOF detection axis, $\mathbf{k}_{\text{TOF}}$. In this reference frame, the z -axis is now parallel to $\mathbf{k}_{\text{TOF}}$ and the polar angles (θ'_t, ϕ'_t) describe the spatial distribution of $\mathbf{v}$ relative to this axis. The azimuthal angle, ϕ'_t , describes all photofragments with the same velocity projection, $\cos \theta'_t$, along the TOF axis. This velocity projection is proportional to the TOF shift and integration

over ϕ'_t gives an expression for the rotational moments in terms of the TOF shift, $x = \cos \theta'_t$, in the dissociation frame, which are given by,¹⁷

$$\begin{aligned} \rho_q^k(J) = & \frac{1}{2} \left((2k+1) \begin{pmatrix} k & 0 & k \\ -q & 0 & q \end{pmatrix} b_0^0(k, k) P_k(x) C_{-q}^k(\theta_D, 0) \right. \\ & \left. + \frac{2}{\sqrt{5}} \sum_{k_1} (2k_1+1) \begin{pmatrix} k_1 & 2 & k \\ -q & 0 & q \end{pmatrix} b_0^2(k_1, k) P_{k_1}(x) C_{-q}^{k_1}(\theta_D, 0) \right), \end{aligned} \quad (3.5)$$

where $P_k(x)$ are Legendre Polynomials of degree k in terms of x . Rotation of these rotational moments by Euler angles of $(\phi_p, \theta_p, \chi_p)$ transforms the dissociation frame rotational moments into the *probe* frame where the z -axis is now parallel to the probe propagation direction, $\mathbf{k}_{\text{probe}}$, and the x -axis is parallel to the probe polarisation vector, $\mathbf{\epsilon}_{\text{probe}}$, for linear polarised probe radiation. This is achieved using Wigner rotation matrices and the resulting probe frame rotational moments, $\rho_q^k(J)'$, are therefore given by,¹⁸

$$\rho_q^k(J)' = \sum_{q'} D_{q',q}^{k*}(\phi_p, \theta_p, \chi_p) \rho_{q'}^k(J), \quad (3.6)$$

where $D_{q',q}^{k*}$ are Wigner rotation matrix elements and the sum is over all allowed values of q' . Here ϕ_p is the angle between $\mathbf{k}_{\text{probe}}$ and $\mathbf{k}_{\text{TOF}}$ projected onto a plane perpendicular to $\mathbf{\epsilon}_{\text{phot}}$, θ_p is the angle between $\mathbf{\epsilon}_{\text{phot}}$ and $\mathbf{k}_{\text{probe}}$, and χ_p is the angle between $\mathbf{\epsilon}_{\text{phot}}$ and $\mathbf{\epsilon}_{\text{probe}}$. These probe frame rotational moments are proportional to the polarisation parameters, A_q^k , discussed in chapter 1. This normalisation is carried out in terms of Biedenharn's angular momentum operators¹⁹ and the factors required are given in table 1 of Ref. 15.

For all the experiments described in this chapter, the photolysis and probe laser beams were counter-propagating and perpendicular to the TOF axis. Consequently, $\theta_p = \pi/2$ and ϕ_p is either $\pi/2$ or undefined. Each experimental geometry is therefore given by the angles θ_D and χ_p defining the angle between $\mathbf{\epsilon}_{\text{phot}}$ and $\mathbf{\epsilon}_{\text{probe}}$ and the TOF axis. The vectors and angles defining each experimental geometry are

illustrated in figure (3.1). For experiments using circular polarised probe light only θ_D is required and χ_p is undefined.

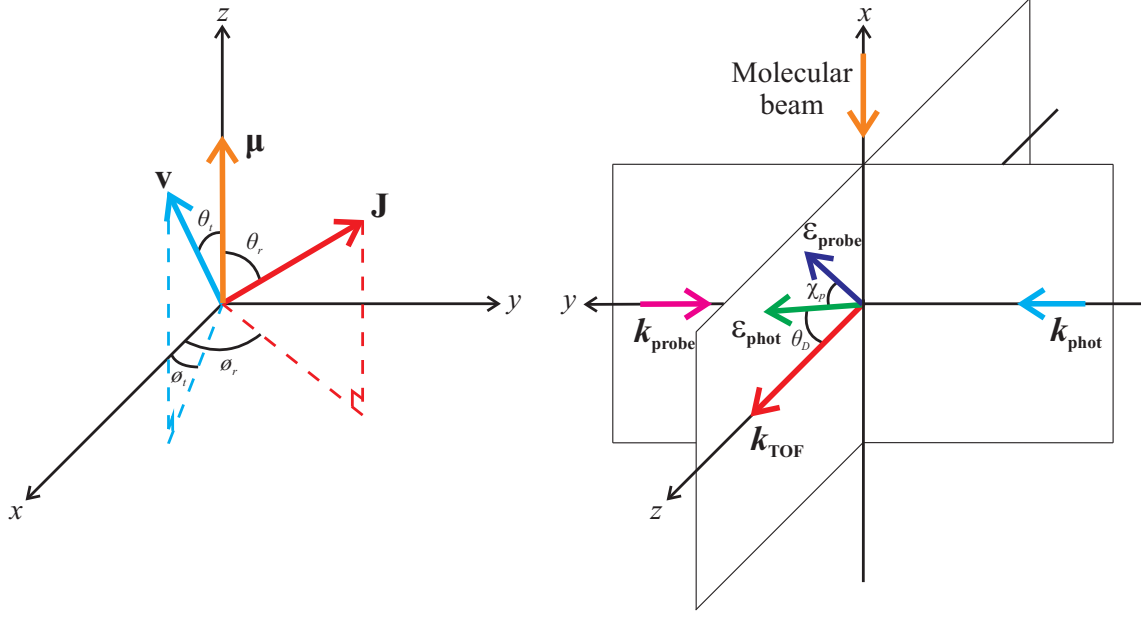


Figure 3.1: Diagrams illustrating the vectors and angles used to define the bipolar moments in the body fixed frame (left) and the different experimental geometries in the laboratory frame (right).

This correlated distribution of $\mathbf{v}$, $\mathbf{J}$ and $\boldsymbol{\mu}$ will now be related to the experimentally measured TOF profiles. Fano and Macek²⁰ have shown how the one-photon absorption intensity depends on the probe frame polarisation parameters, A_q^k . This is given by,

$$I(J) = C_{\text{det}} \left(A_0^0(J) - \frac{1}{2} h^{(2)}(J) [A_0^2(J) - 3 \cos(2\beta) A_{2+}^2(J)] + \frac{3}{2} \sin(2\beta) h^{(1)}(J) A_0^1(J) \right), \quad (3.7)$$

where C_{det} is a detection constant and β is an angle defining the polarisation of the probe laser beam, with $\beta = 0$ corresponding to linear polarised light and $\beta \pm \pi/4$ corresponding to circular polarised light. The coefficients, $h^{(k)}$, are depolarisation factors which reflect the amount of information lost during a particular transition. These factors depend on the specific transition used to probe the photofragment

and are given in table 3.1.^{17,18,20} By using equation (3.6) along with the correct normalisation factors, the relevant polarisation parameters may be calculated in terms of the bipolar moments and the TOF shift. Substituting these into equation (3.7) gives an expression for the intensity of the measured TOF profiles in terms of bipolar moments, assuming that the ionisation step occurs isotropically.

Table 3.1: Expressions used to calculate the depolarisation factors, $h^{(k)}$, appearing in equation (3.7) for different absorption branches. Here J refers to the lower energy level of the probe transition.

Branch	$h^{(1)}(J)$	$h^{(2)}(J)$
P	$-(J+1)[J(J+1)]^{-1/2}$	$-(J+1)/(2J-1)$
Q	$[J(J+1)]^{-1/2}$	1
R	$(J+1)[J(J+1)]^{-1/2}$	$-J/(2J+3)$

The calculated TOF profiles will, in principle, depend on a large number of bipolar moments, however, symmetry constraints limit the number that contribute to the measured profiles. The bipolar moments defined in the body-fixed frame have cylindrical symmetry about $\boldsymbol{\mu}$. Therefore, only bipolar moments which are independent of the azimuthal angle about $\boldsymbol{\mu}$ will affect the measured profile and therefore only bipolar moments of projection $Q = 0$ need to be considered. Additionally, one-photon probing limits the measureable bipolar moments to $0 \leq K \leq 2$ and $0 \leq k_2 \leq 2$ as these are the only moments which contribute to the polarisation parameters in equation (3.7). K must be even for linear polarised photolysis due to the dipolar nature of the linear photolysis electric vector and restricts the measureable moments to those which are symmetric along z -axis in the body-fixed frame. Similarly, k_2 must be even for linear polarised probe light, whilst if circular polarised probe light is used k_2 may take odd values. The values k_1 may take are determined by the triangle rule, where $|K - k_2| \leq k_1 \leq |K + k_2|$. Applying all of these constraints we find that for one-photon probing with linear polarised photolysis and probe light

only five bipolar moments need to be considered; $\beta_0^2(2, 0)$, $\beta_0^2(0, 2)$, $\beta_0^0(2, 2)$, $\beta_0^2(2, 2)$ and $\beta_0^2(4, 2)$. If circular polarised probe light is used an additional bipolar moment is required, $\beta_0^2(2, 1)$.

We therefore find that the expression for the TOF profile for one-photon linear polarised probing following linear photolysis is given by,

$$I = g_0 + g_2 P_2(x) + g_4 P_4(x), \quad (3.8)$$

where $P_k(x)$ are Legendre polynomials of degree k in terms of the TOF shift, x . g_k are coefficients which will depend on the depolarisation factors, $h^{(k)}$, the two angles describing the experimental geometry, θ_D and χ_p , and the five bipolar moments given previously. Exact expressions for the coefficients, g_k , are given in Appendix A. This expression is then convoluted with the functions describing the effects of core extraction and the temporal width of the probe laser described in the previous chapter to give a simulation of the measured TOF profile. This expression is valid for probing photofragments using $(1 + n)$ REMPI schemes, as will be used in this chapter to probe NO photofragments, in later chapters $(2 + 1)$ REMPI schemes will be used to probe the photofragments and equation (3.8) will depend on higher order Legendre polynomials. In general, the maximum order of Legendre polynomials appearing in the expression for the measured TOF profile is equal to $2(p + m)$, where p is the number of photolysis photons and m is the number of probe photons.

The measureable bipolar moments all have distinct physical meanings. The three lower order moments, $\beta_0^2(2, 0)$, $\beta_0^2(0, 2)$ and $\beta_0^0(2, 2)$, represent the $\boldsymbol{\mu}-\mathbf{v}$, $\boldsymbol{\mu}-\mathbf{J}$ and $\mathbf{v}-\mathbf{J}$ vector correlations respectively. They have limiting values of $-1/2$ and $+1$ which correspond to perpendicular and parallel arrangements of these vectors respectively. The $\beta_0^2(2, 0)$ bipolar moment may be converted to the translational anisotropy parameter, β , discussed in chapter 1 by the relation $\beta = 2\beta_0^2(2, 0)$. The higher order alignment bipolar moments, $\beta_0^2(2, 2)$ and $\beta_0^2(4, 2)$, represent more complicated $\boldsymbol{\mu}-\mathbf{v}-\mathbf{J}$ triple vector correlations. The bipolar moment $\beta_0^2(2, 1)$ describes the orientation of $\mathbf{J}$ with respect to an axis perpendicular to the plane defined by $\boldsymbol{\mu}$

and $\mathbf{v}$. It takes positive values if $\mathbf{J}$ is orientated parallel to $\mathbf{v} \times \boldsymbol{\mu}$ or negative values if $\mathbf{J}$ is antiparallel to $\mathbf{v} \times \boldsymbol{\mu}$ and when $\mathbf{v}$ is at 45° to $\boldsymbol{\mu}$ may take maximum limiting values of ± 1 . In the high- J limit, these six bipolar moments are all related to expectation values of the body-fixed frame angles defined previously.¹⁵ The physical interpretations of the three lower order alignment bipolar moments and the orientation moment are summarised in table 3.2, where ω_{tr} is the angle between $\mathbf{v}$ and $\mathbf{J}$. For the higher order moments their dependence on the body-fixed frame angles is more complicated and the expectation values for these moments may be found in table II of Ref. 15.

Table 3.2: A summary of the physical interpretation of the three lower order alignment bipolar moments and the orientation bipolar moment.

Bipolar moment	Vector correlation	Range	Expectation value argument
$\beta_0^2(2, 0)$	$\boldsymbol{\mu} - \mathbf{v}$	-1/2 to 1	$P_2(\cos \theta_t)$
$\beta_0^2(0, 2)$	$\boldsymbol{\mu} - \mathbf{J}$	-1/2 to 1	$P_2(\cos \theta_r)$
$\beta_0^0(2, 2)$	$\mathbf{v} - \mathbf{J}$	-1/2 to 1	$P_2(\cos \omega_{tr})$
$\beta_0^2(2, 1)$	$\boldsymbol{\mu} - \mathbf{v} - \mathbf{J}$ orientation	-1 to 1	$-2 \sin \theta_t \cos \theta_t \sin \theta_r \sin(\phi_r - \phi_t)$

It should be noted that the derivation of the bipolar moments used in this work relies on being able to describe the spatial distribution of $\mathbf{J}$ about $\boldsymbol{\mu}$ in terms of spherical harmonics. This is only valid if $\mathbf{J}$ is high enough so that it may be treated classically as a vector. Additionally, the transformation from the body-fixed frame to the dissociation frame is only unambiguous if only one transition is involved. These issues have been resolved by Costen *et al.*²¹ who have derived expressions for bipolar moments appropriate for low- J photofragments by treating $\mathbf{J}$ as a spherical tensor. These bipolar moments are referenced relative to $\boldsymbol{\epsilon}_{\text{phot}}$ instead of $\boldsymbol{\mu}$ for linear polarised photolysis which is more appropriate for multiple surface dissociations. In this work, however, only high- J NO fragments resulting from dissociation following excitation to a single ²B₂ surface will be probed and therefore the bipolar moments derived previously in this section are appropriate.

3.2.2 Extracting the bipolar moments

In order to accurately extract all of the bipolar moments, TOF profiles were taken in multiple geometries which were chosen to be particularly sensitive to individual parameters. Generally, a complimentary pair of geometries was chosen whereby one laser had a fixed linear polarisation and the second laser was either switched between horizontal and vertical linear polarisation or left and right circular polarisation using the PEM described in chapter 2. Most of the bipolar moments were determined by fitting to the shape of the TOF profiles. For this procedure, the experimentally measured profiles were area normalised and symmetrised following background subtraction of the probe-only one-laser signal. Simulations of the TOF profiles were generated using equation (3.8) and subsequently convoluted with functions accounting for core extraction and the temporal width of the probe laser. These simulations were then fit to the sum and difference of the experimental profiles using a multi-variable least squares fit using a trust-region reflective algorithm available as a built in function in Matlab to extract the required parameter.^{22,23} All of the experimental geometries were chosen to isolate individual parameters but were also weakly dependent on other parameters. In each case the additional parameters were either constrained to a value measured in a previous geometry or were estimated classically. This was achieved by converting the already determined bipolar moments into the corresponding body-fixed frame angles using the relations discussed in the previous section and then using these angles to predict the unknown bipolar moment. If an angle could not yet be determined it was estimated using the simple impulsive model described in section 3.3. This is clearly a very approximate determination of the extra bipolar moments contributing to the lineshapes but the errors associated with this method are expected to be small since the dependence of the profile on these moments is much smaller than the bipolar moment optimised by the multivariable fit. Each of the geometries used in this chapter will now be considered and it will be demonstrated how they enable all of the bipolar moments to be determined.

3.2.2.1 Experimental parameters

The experimental parameters used to model the core extraction and the temporal width of the probe laser, σ , C_1 and C_2 , described in the previous chapter were determined from profiles recorded in a geometry, G_1 , where both photolysis and probe lasers are linearly polarised at the magic angle, 54.7° , to the TOF axis ($\theta_D = 54.7^\circ$, $\chi_p = 0^\circ$). The shape of the TOF profile taken in this geometry has a minimal dependence on the bipolar moments and will therefore be mostly dependent on the experimental effects of core extraction and the temporal width of the probe laser and fitting simulations to profiles taken in this geometry may be used to determine the values of σ , C_1 and C_2 . Using equation (3.8) to calculate the expression for the TOF profile taken in this geometry shows that the higher order, $\beta_0^2(4, 2)$, bipolar moment does have a small contribution to the overall lineshape. However, fits were performed ignoring this contribution since its small contribution to the overall lineshape was found to not affect the values of the returned σ , C_1 and C_2 parameters.

3.2.2.2 $\beta_0^2(0, 2)$: the μ -J correlation

The value of $\beta_0^2(0, 2)$ was determined *via* a pair of geometries, G_2 , taken with the photolysis laser horizontally polarised whilst the probe laser was switched between horizontal and vertical polarisation ($\theta_D = 0^\circ$, $\chi_p = 0/90^\circ$). Expressions for the TOF profiles taken in these geometries, I_{HH} and I_{HV} , where the subscripts H or V refer to the horizontal or vertical polarisation of the photolysis and probe laser beams respectively, can be calculated using equation (3.8) and are given by,

$$\begin{aligned}
 I_{HH} = 1 + \frac{4}{5}h^{(2)}(J)\beta_0^2(0, 2) + \left(2\beta_0^2(2, 0) + 2h^{(2)}(J)\beta_0^0(2, 2) - \frac{8}{7}h^{(2)}(J)\beta_0^2(2, 2)\right)P_0^2(x) \\
 + \frac{72}{35}h^{(2)}(J)\beta_0^2(4, 2)P_0^4(x),
 \end{aligned}
 \tag{3.9}$$

$$I_{HV} = 1 - \frac{2}{5}h^{(2)}(J)\beta_0^2(0, 2) + \left(2\beta_0^2(2, 0) - h^{(2)}(J)\beta_0^0(2, 2) + \frac{4}{7}h^{(2)}(J)\beta_0^2(2, 2)\right)P_0^2(x) - \frac{36}{35}h^{(2)}(J)\beta_0^2(4, 2)P_0^4(x). \quad (3.10)$$

It is clear that the influence of the $\beta_0^2(0, 2)$ parameter on this profile is not dependent on the TOF shift, x . This means that the $\beta_0^2(0, 2)$ bipolar moment only affects the intensity and not the shape of the TOF profiles. By measuring the integrated intensity of profiles measured in these two geometries the value of $\beta_0^2(0, 2)$ can therefore be determined. The value of $\beta_0^2(0, 2)$ is therefore simply related to the ratio of the integrated intensity of TOF profiles taken in these geometries, $R = I_{HV}/I_{HH}$, by,

$$\beta_0^2(0, 2) = \frac{5}{4} \frac{(R - 1)}{h^{(2)}(J) (1 + R/2)}. \quad (3.11)$$

3.2.2.3 $\beta_0^2(2, 0)$: the μ -v correlation

The value of $\beta_0^2(2, 0)$ was determined *via* a pair of geometries, G_3 , taken with the probe laser polarised at the magic angle, whilst the photolysis laser was switched between horizontal and vertical polarisation ($\theta_D = 0/90^\circ$, $\chi_p = 54.7^\circ - 35.3^\circ$). Expressions for the TOF profiles taken in these geometries, I_{Hma} and I_{Vma} , calculated using equation (3.8) are given by,

$$I_{Hma} = 1 + 2\beta_0^2(2, 0)P_0^2(x), \quad (3.12)$$

$$I_{Vma} = 1 + \frac{2}{5}h^{(2)}(J)\beta_0^2(0, 2) + \left(-\beta_0^2(2, 0) + \frac{4}{7}h^{(2)}(J)\beta_0^2(2, 2)\right)P_0^2(x) + \frac{6}{35}h^{(2)}(J)\beta_0^2(4, 2)P_0^4(x). \quad (3.13)$$

In this case the $\beta_0^2(2, 0)$ parameter does not affect the intensity of the measured profiles and is determined by simultaneously fitting to the sum and difference of area normalised profiles taken in these geometries. Clearly, the $\beta_0^2(2, 0)$ parameter may also be determined by simply fitting equation (3.12) to the experimental profile taken with the probe laser polarised at the magic angle and the photolysis

laser horizontally polarised since this profile only depends on the $\beta_0^2(2, 0)$ bipolar moment. The determination of the translational anisotropy by fitting to sum and difference profiles is preferred, however, since this will minimise the influence of the experimental parameters. Additionally, in later chapters, where $(2 + 1)$ REMPI schemes are used, I_{Hma} will depend on more than just the translational anisotropy and fitting to sum and difference profiles will be necessary.

3.2.2.4 $\beta_0^0(2, 2)$: the $\mathbf{v-J}$ correlation

The value of $\beta_0^0(2, 2)$ was determined *via* a pair of geometries, G_4 , taken with the photolysis laser polarised at the magic angle, whilst the probe laser was switched between horizontal and vertical polarisation ($\theta_D = 54.7^\circ$, $\chi_p = -54.7/35.3^\circ$). Expressions for the TOF profiles taken in these geometries, I_{maH} and I_{maV} , calculated using equation (3.8) are given by,

$$I_{maH} = 1 + \left(-\frac{2}{3}h^{(2)}(J)\beta_0^0(2, 2) + \frac{16}{21}h^{(2)}(J)\beta_0^2(2, 2) \right) P_0^2(x) + \frac{16}{21}h^{(2)}(J)\beta_0^2(4, 2)P_0^4(x), \quad (3.14)$$

$$I_{maV} = 1 + \frac{2}{5}h^{(2)}(J)\beta_0^2(0, 2) + \left(\frac{5}{3}h^{(2)}(J)\beta_0^0(2, 2) - \frac{4}{21}h^{(2)}(J)\beta_0^2(2, 2) \right) P_0^2(x) - \frac{62}{105}h^{(2)}(J)\beta_0^2(4, 2)P_0^4(x). \quad (3.15)$$

In this case the $\beta_0^0(2, 2)$ parameter may be determined by simultaneously fitting to the sum and difference of area normalised profiles taken in these geometries.

3.2.2.5 Higher order moments: the $\mu\text{-v-J}$ correlation

Values of the higher order bipolar moments, $\beta_0^2(2, 2)$ and $\beta_0^2(4, 2)$, were determined by fitting to the the sum and difference profiles taken in geometry pair G_2 . These profiles aren't particularly sensitive to these moments but once the values for the other bipolar moments have been determined they may be constrained so that the

fitting equation only depends on the $\beta_0^2(2, 2)$ and $\beta_0^2(4, 2)$ moments.

3.2.2.6 $\beta_0^2(2, 1)$: **J** orientation

The value of the orientation bipolar moment, $\beta_0^2(2, 1)$, was determined *via* a pair of geometries, G_5 , with the photolysis laser linearly polarised at 45° to the TOF axis and the probe laser switched between left and right circular polarisation ($\theta_D = 45^\circ$). There is no net orientation of the photofragment angular velocity in the laboratory frame for linear polarised photolysis due to the cylindrical symmetry of the system and $\beta_0^2(2, 1)$ will therefore only affect the shape and not the intensity of the TOF profiles taken in this geometry. An expression for the TOF profile taken in this geometry pair, $I_{45\text{circ}}$, is calculated from equation (3.8),

$$\begin{aligned} I_{45\text{circ}} = & 1 + \frac{1}{5}h^{(2)}(J)\beta_0^2(0, 2) \\ & + \left(\frac{1}{2}\beta_0^2(2, 0) - \frac{9}{8}h^{(1)}(J)\beta_0^2(2, 1)\sin 2\beta + \frac{1}{2}h^{(2)}(J)\beta_0^0(2, 2) + \frac{1}{7}h^{(2)}(J)\beta_0^2(2, 2) \right) P_0^2(x) \\ & + \frac{27}{140}h^{(2)}(J)\beta_0^2(4, 2)P_0^4(x), \end{aligned} \quad (3.16)$$

where $\beta = +\pi/4$ and $\beta = -\pi/4$ for left and right circularly polarised probe light respectively.²⁴ A difference in the TOF profiles taken with left and right circular polarised light will therefore result from non-zero values of $\beta_0^2(2, 1)$ and this parameter is determined by fitting to the difference of area normalised profiles taken in this geometry pair.

For the dissociation of NO₂, whilst there is no net orientation of the photofragment angular velocity in the laboratory frame there may be an orientation of **J** in the $\boldsymbol{\mu}$ – $\mathbf{v}$ plane resulting from the impulse imparted on the departing diatom as the molecule dissociates. To illustrate how experimental geometry G_5 provides maximum sensitivity to this orientation moment we will consider an ensemble of photofragments produced with a single velocity, $\mathbf{v}$, at a specific angle to $\boldsymbol{\mu}$, with their angular momentum, **J**, at a fixed orientation in the body-fixed frame. For

a cylindrically symmetric dissociation about μ , the spatial distribution of these photofragments may be illustrated by a recoil velocity sphere of radius $|\mathbf{v}|$ as shown in figure 3.2. The oriented angular momentum, $\mathbf{J}$, points tangentially to the sphere with photofragments in either hemisphere rotating in the opposite sense around the symmetry axis, μ . Figure 3.2 shows the distribution of photofragments for the two cases when μ is parallel and at 45° to the TOF axis, $\mathbf{k}_{\text{TOF}}$. It is clear that when μ is parallel to $\mathbf{k}_{\text{TOF}}$, for each set of photofragments with the same velocity projection along the TOF axis there is an equal number of photofragments with $\mathbf{J}$ oriented parallel or antiparallel to any specific direction. The same situation will also occur if μ is perpendicular to the TOF axis. In order to break this symmetry, the sphere of photofragments needs to be oriented so that its symmetry axis is at an angle between 0° and 90° to $\mathbf{k}_{\text{TOF}}$. In this case, for each set of photofragments with the same velocity projection along the TOF axis there is now a net orientation of $\mathbf{J}$. Clearly, this sensitivity is maximised when the symmetry axis is at 45° to the TOF axis, as shown in figure 3.2. If we assume ϵ_{phot} is parallel to μ it is clear that an experimental geometry where ϵ_{phot} is set at 45° to the TOF axis will achieve maximum sensitivity to the orientation of photofragment angular momentum.

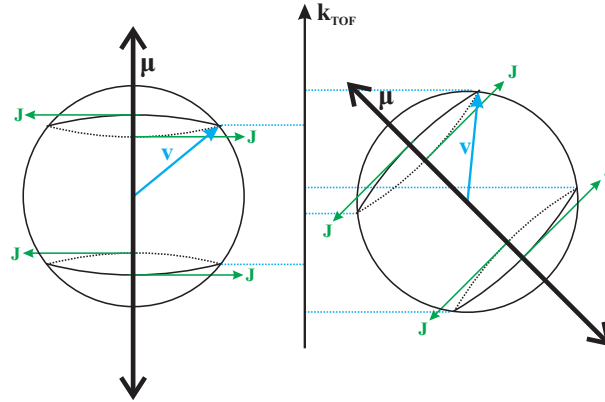


Figure 3.2: Diagrams showing a cylindrically symmetric distribution of photofragments with μ orientated parallel (left) and at 45° to the TOF axis (right), illustrating the sensitivity of the experimental geometry in determining the orientation of photofragments. Figure adapted from Ref. 24.

3.2.3 Experimental uncertainty

The parameters reported in this chapter were mostly determined from fits to the sum and difference of experimental profiles averaged over 3000 laser shots. The experimental uncertainty of the parameters returned from these parameter optimised fits was determined using the technique of Monte-Carlo sampling similar to that employed by Costen *et al.*^{23,25} Here it is assumed that the deviation of the experimental data set from the best-fit simulation is a good approximation to the deviation of that data set from the TOF profile that would be measured in the absence of experimental noise. The standard deviation of the residuals of the experimental data set to the best-fit simulation are used to generate synthetic noisy profiles and the fitting procedure is repeated for each of these profiles. The quoted errors for each parameter are twice the standard deviation of the values obtained from fitting to the synthetic profiles. In all cases 1000 synthetic data sets were generated, which was found to ensure convergence of the returned errors to within the precision with which they are presented.²³ For the $\beta_0^2(2,0)$ moment, where its value is determined from the integrated areas of the profiles, the quoted errors are twice the standard deviation of the values obtained from 10 separate experiments.

3.3 The impulsive model

In order to illustrate the information which may be obtained on the dissociation process through the measurement of bipolar moments, the dissociation of a cold triatomic molecule based on a classical *impulsive* model will first be considered. The impulsive model assumes that for a triatomic molecule, ABC, a repulsive force develops instantaneously between the departing atom, A, and the atom it is bonded to, B, which acts directly along the dissociating bond. This repulsion generates a torque which results in rotational excitation of the departing molecule, BC.^{26,27} For the photodissociation of NO₂ at 320 nm studied in this work, the initial photon absorption results in an ${}^2\text{B}_2 \leftarrow \text{X } {}^2\text{A}_1$ excitation. For an electronic transition to be

fully allowed the transition dipole moment integral must be totally symmetric and therefore for an ${}^2B_2 \leftarrow X {}^2A_1$ excitation the transition dipole moment must have 2B_2 symmetry. Inspection of the group table for a C_{2v} molecule shows that this corresponds to a transition dipole moment which is perpendicular to the molecule's principle rotation axis and lies in the plane of the molecule. Figure 3.3 shows the arrangement of vectors predicted by the impulsive model for this photodissociation process, where $\mathbf{J}$ is pointing out of the page. It is clear from the figure that the impulsive model predicts perpendicular $\boldsymbol{\mu}-\mathbf{J}$ and $\mathbf{v}-\mathbf{J}$ correlations, corresponding to $\beta_0^2(0,2) = -0.5$ and $\beta_0^2(2,2) = -0.5$. The $\boldsymbol{\mu}-\mathbf{v}$ correlation will depend on the molecular bond angle, α , at the moment of dissociation and the measured translational anisotropy parameter, $\beta (= 2\beta_0^2(2,0))$, for the dissociation of a triatomic molecule with a particular value of α within the axial-recoil approximation is given by,

$$\beta = 2P_2 \left(\cos \left(\frac{\pi - \alpha}{2} \right) \right). \quad (3.17)$$

It is therefore predicted that $\beta = 1.55$, assuming that NO₂ dissociates from its ground state equilibrium geometry with $\alpha = 134.25^\circ$. This model may also be used to predict the angular momentum orientation, $\beta_0^2(2,1)$. As can be seen from figure 3.3, for a pure impulsive model the rotation of the NO molecule produced will be such that $\mathbf{J}$ is parallel to $\mathbf{v} \times \boldsymbol{\mu}$ and therefore $\beta_0^2(2,1)$ takes its limiting value of 0.72.

This impulsive model is clearly very approximate, making many assumptions on the dissociation process. The main problem with the impulsive model is that it assumes that the only source of angular momentum is from the impulsive force of the breaking bond. For the direct dissociation of a triatomic molecule a major source of torque which will cause significant deviations from the impulsive model predictions is anisotropy in the angular potential. For example, dissociation of water at 157 nm occurs adiabatically *via* the A state and yields rotationally cold OH ${}^2\Pi$ fragments²⁸ whilst dissociation at 122 nm occurs *via* the B state and yields

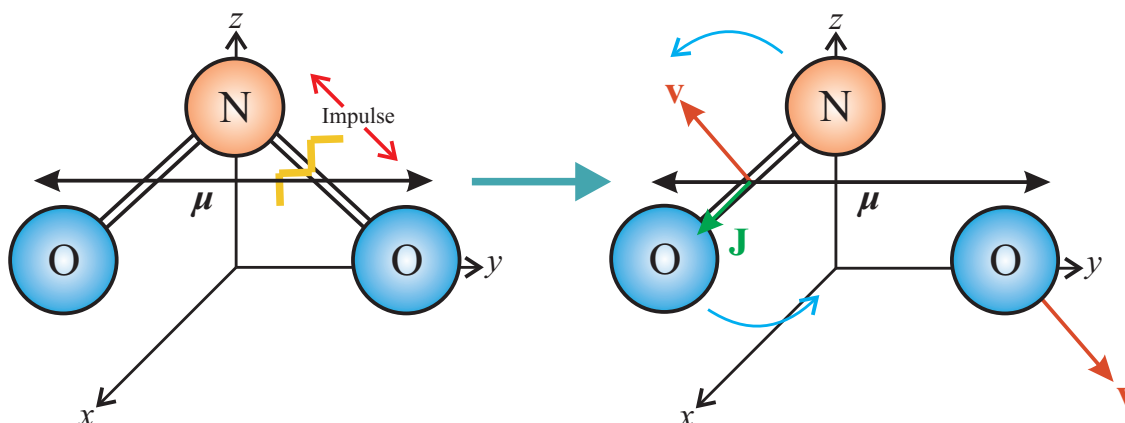


Figure 3.3: Diagram illustrating the arrangement of vectors predicted by the impulsive model for the dissociation of NO₂ at 320 nm.

rotationally excited OH $^2\Sigma^+$ fragments.²⁹ Schematic cuts through the PESs for the two states reveals that the B state has a minimum at linearity, far from the initially excited bond angle, resulting in strong torque during dissociation which causes the extra rotational excitation.³⁰ The dissociation of NO₂ studied in this chapter is not direct but a vibrational predissociation from a barrierless PES. In this case, the main additional source of diatom angular momentum will be due to bending motion of the parent molecule as it dissociates.⁹ As mentioned in the introduction, the NO₂ molecule accesses the conical intersection with a smaller bond angle than the ground state equilibrium bond angle and therefore a symmetric bend will be excited as the molecular bond angle opens towards the ground state equilibrium geometry. This bending motion will have a frequency of $< 20 \text{ cm}^{-1}$ close to the dissociation threshold⁹ and will increase as the excess dissociation energy increases and the transition state tightens. This has been approximated to be 100 cm^{-1} at 338.9 nm³¹ and will therefore provide a significant torque on the departing NO molecules probed in this work, which will counter the torque generated from the dissociation impulse. An additional source of angular momentum which will cause deviations from the impulsive model predictions is rotational motion of the parent molecule prior to dissociation. The rotational temperature of the molecular beam of NO₂, which will be discussed in the next section, is non-zero and therefore rotation of the parent molecule will

affect the measured vector correlations. Despite these shortcomings, the impulsive model does provide a useful starting point for interpreting the measured vector correlations and deviations from the impulsive model predictions will be discussed in more detail later.

3.4 Molecular beam rotational temperature

3.4.1 Determining the rotational temperature of a molecular beam

As mentioned in the previous section, rotational motion of the parent molecule prior to dissociation will affect the measured vector correlations. It is therefore important to characterise the rotational energy distribution of the molecules used in these experiments. This is achieved by determining an effective rotational temperature, T_{rot} , of the molecular beam assuming that the rotational levels are well described by the Boltzmann distribution,

$$P(J, K) = \frac{g(J, K) \exp\left(-\frac{E_{\text{rot}}}{k_B T_{\text{rot}}}\right)}{q_{\text{rot}}}. \quad (3.18)$$

Here $P(J, K)$ is the probability that a molecule with a rotational partition function, q_{rot} , will be in a rotational state with quantum numbers J and K , degeneracy $g(J, K)$ and energy E_{rot} (at a given T_{rot}). Determination of the rotational temperature of the molecular beam was achieved by analysing rotationally resolved REMPI spectra of NO. A sample of 20% NO (Aldrich, 99.5%) in helium at a backing pressure of 300 Torr entered the chamber *via* a pulsed valve under conditions identical to those described in chapter 2. A laser operating at wavelengths around 329 nm was then used to obtain a (2+1) REMPI spectrum of the NO X $^2\Pi_{\Omega}$ molecules excited *via* the E $^2\Sigma^+$ state.

NO molecules in their ground X $^2\Pi_{\Omega}$ state at low rotational excitation are well described by Hund's case (a). In this coupling scheme, the electronic orbital angu-

lar momentum, $\mathbf{L}$, is strongly coupled to the internuclear axis through electrostatic forces. The electronic spin angular momentum, $\mathbf{S}$, is strongly coupled to $\mathbf{L}$ through spin orbit coupling and therefore both $\mathbf{L}$ and $\mathbf{S}$ precess around the internuclear axis with well defined projections along this axis denoted Λ and Σ respectively. The angular momentum of the rotating nuclei, $\mathbf{R}$, couples to the vector, $\mathbf{\Omega} = \mathbf{\Lambda} + \mathbf{\Sigma}$, to form the resulting total angular momentum, $\mathbf{J}$. The arrangement of vectors is illustrated in figure 3.4. For NO in the ground state $\Lambda = \pm 1$ and $\Sigma = \pm 1/2$ which couple to form a total angular momentum projection of $\Omega = \pm 1/2, \pm 3/2$. The ground state is therefore split into two spin orbit components, ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$, denoted F_1 and F_2 respectively, separated by an energy of approximately 121.1 cm^{-1} .³² For a non-rotating molecule the energy of states with $\pm\Omega$ are degenerate, however, this degeneracy is lifted for a rotating molecule and a small splitting, known as lambda-doubling, occurs for states with the same value of $\mathbf{J}$. Here we will be probing NO molecules in low- J levels of the X ${}^2\Pi_{\Omega}$ state and are therefore well described by Hund's case (a).

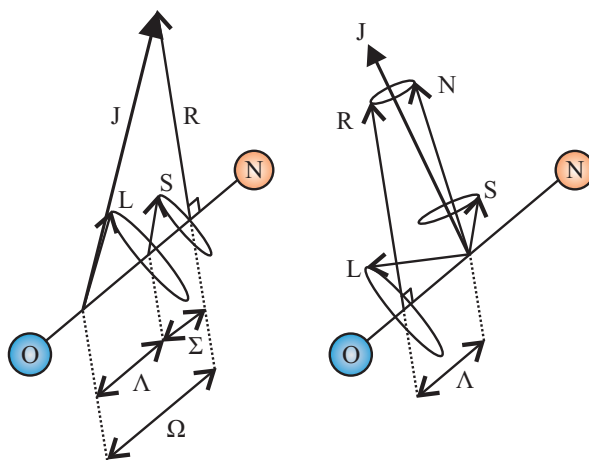


Figure 3.4: Diagram illustrating the arrangement of vectors within the Hund's case (a) (left) and Hund's case (b) (right) coupling schemes.

As the molecule rotates faster the angular momentum of the rotating nuclei, $\mathbf{R}$, starts to become more dominant and the Hund's case (b) coupling scheme becomes more appropriate. $\mathbf{L}$ is still strongly coupled to the internuclear axis with a projec-

tion, $\mathbf{A}$, which couples with $\mathbf{R}$ to form a resultant angular momentum, $\mathbf{N}$, the total angular momentum not including electron spin. $\mathbf{S}$, which was weakly coupled to the internuclear axis through spin orbit coupling in Hund's case (a), is now decoupled from the internuclear axis and instead couples to $\mathbf{N}$ to form the total angular momentum, $\mathbf{J}$. This coupling scheme is also illustrated in figure 3.4. When probing the NO X $^2\Pi_\Omega$ molecules produced following the photodissociation of NO₂ at 320 nm photofragments in high- J levels will be detected. These are well described by Hund's case (b) and in this case the labels F₁ and F₂ refer to levels where $J = N + \frac{1}{2}$ and $J = N - \frac{1}{2}$ respectively. For all states with $\Lambda = 0$, like the E $^2\Sigma^+$ state, there is no component of $\mathbf{L}$ to couple $\mathbf{S}$ to the internuclear axis and therefore the molecule is described by Hund's case (b) for all J states.

Assuming a Boltzmann distribution of rotational levels, the integrated intensity, $I_{J'J''}$, of a rotational transition can be written as,³³

$$I_{J'J''} = Cg(J'')S(J'J'')\exp\left(-\frac{E_{\text{rot}}}{k_B T_{\text{rot}}}\right), \quad (3.19)$$

where J'' and J' are rotational quantum numbers for the lower and upper states respectively. C is a constant which incorporates all the factors which are independent of rotational quantum number, such as Franck-Condon factors, number densities, laser intensity *etc.* and is the same for all transitions within a particular branch. $S(J'J'')$ is the Hönl-London line-strength factor for the transition which are tabulated for two-photon transitions by Bray and Hochstasser.³⁴ Therefore a plot of $\ln\left(\frac{I_{J'J''}}{g(J'')S(J'J'')}\right)$ against $\frac{E_{\text{rot}}}{k_B}$ for a series of transitions within the same rotational branch will yield a straight line plot with a gradient equal to $-\frac{1}{T_{\text{rot}}}$. This analysis requires the measurement of several transitions originating from different J'' within the same rotational branch which aren't overlapped with any other rotational transitions. A spectral simulation of the E $^2\Sigma^+ \leftarrow \leftarrow$ X $^2\Pi_\Omega$ absorption band was generated using the PGopher spectral simulation program^{32,35,36} and it was determined that the O₁₂ sub-branch, where the subscripts denote the upper and lower F component, had a series of suitable isolated transitions. Figure 3.5 shows the (2+1) REMPI

spectrum recorded in the wavelength region (329.41 – 329.64) nm and a Boltzmann plot of the isolated transitions indicated on the spectrum reveals the rotational temperature of the molecular beam to be 140 ± 10 K. Also shown in figure 3.5 is the spectral simulation over the same wavelength region assuming this experimentally determined rotational temperature of 140 K.

Impurities such as NO₂ and N₂O will be present in the NO gas taken directly from the gas cylinder. Rotationally hot NO photofragments may be produced from the photodissociation of these impurities and this will result in raising the apparent rotational temperature of the molecular beam. Attempts were therefore made to remove these impurities which were frozen out of the NO gas and held in a glass bulb using a liquid nitrogen / 2-methyl butane slush bath (-160°C). Despite these efforts, some residual impurities may still remain in the probed NO sample and the measured rotational temperature may therefore be slightly higher than the true molecular beam temperature. For example, the very weak transition indicated by the asterisk in figure 3.5 is the O₁₂($N = 31$) transition and its presence in the measured spectrum is a result of these rotationally hot NO photofragments.

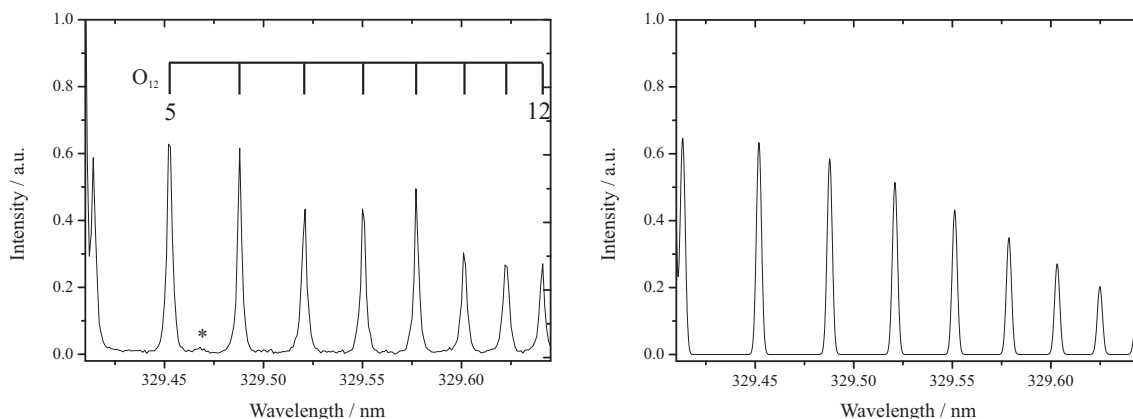


Figure 3.5: (2+1) REMPI spectrum of the E $^2\Sigma^+ \leftarrow \leftarrow X$ $^2\Pi$ absorption band of NO using the unskimmed molecular beam (left) and a simulation of this band using the rotational temperature determined from a Boltzmann plot (right). The asterisk indicates a high- N transition resulting from the photodissociation of impurities in the NO sample, as discussed in the text.

3.4.2 Rotationally cooling the molecular beam

In order to gain as clear a picture as possible of the photodissociation process from photofragment angular momentum alignment measurements, any additional sources of angular momentum not produced by the dissociation process should be minimised. In particular, rotational motion of the parent molecule prior to dissociation will affect the measured vector correlations and should therefore be minimised. The rotational temperature was therefore reduced by incorporating a two-stage pumping system and a skimmer into the experimental setup described in chapter 2 and is illustrated in figure 3.6.

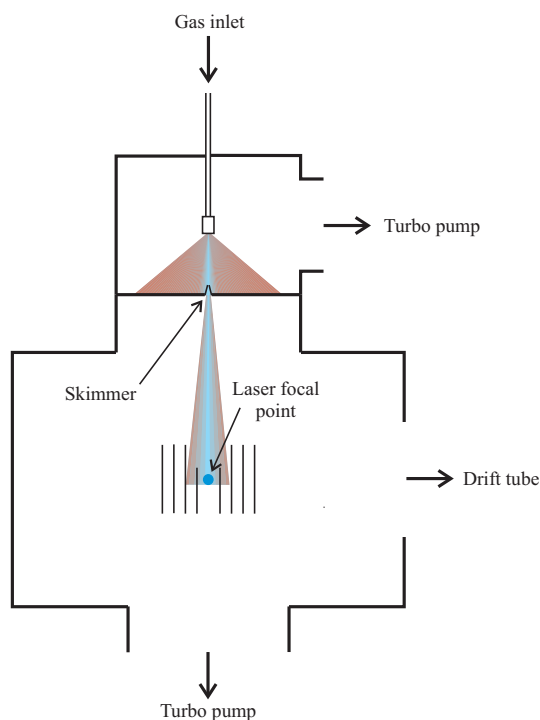


Figure 3.6: Diagram illustrating the modifications to the experimental setup to enable further rotational cooling of the molecular beam. In the figure red and blue areas represent rotationally hot and cold parts of the molecular beam respectively.

Instead of the pulsed valve being in the source region of the TOF spectrometer, it was raised above the main chamber into an additional chamber. This chamber was separated from the main TOF chamber by a skimmer (Beam Dynamic, Inc., 0.5 mm

diameter) and with the pulsed valve off this chamber was kept at typical pressures of 2×10^{-8} Torr using another turbo-molecular pump (Leybold TMP 600C) backed by a rotary pump (Leybold D40B). The small aperture of the skimmer means higher backing pressures can be applied to the pulsed valve than in the unskimmed setup without increasing the pressure in the main chamber of the TOF spectrometer above suitable operating pressures, which enables a greater degree of rotational cooling of molecules as they form a supersonic expansion from the pulsed valve. For the experiments described in this chapter, increased backing pressures of 760 Torr of 5% NO₂ (Aldrich, 99.5%) in He was used with 5% O₂ added to suppress any NO impurities in the NO₂. Care must be taken when using increased backing pressures as this may result in formation of clusters in the molecular beam, however checks were made that changing the backing pressure did not affect the shapes of the measured TOF profiles to ensure that clusters were not affecting the measured profiles.

An additional advantage of using a skimmed molecular beam source is that it allows the rotationally coldest section of the molecular beam to be selected. The structure of the supersonic expansion is that of an isentropic core surrounded concentrically by a shock boundary and a shock front, called the Mach disc, formed perpendicular to the direction of the expansion.^{37,38} These shock regions originate from molecular collisions with background gas and will therefore reheat the cooled expansion. The Mach disc under these conditions will be longer than that calculated in chapter 2 due to the higher backing pressure and is calculated to occur 2.9 m away from the pulsed valve.³⁷ Therefore, even with the pulsed valve raised above the main chamber the molecular beam will reach the centre of the source region well before this point. By placing a skimmer in the path of the molecular beam the isentropic core is selectively isolated and the rotationally coldest part of the expansion continues to the source region in the main chamber. As well as cooling the molecular beam, this selective isolation of the isentropic core produces a better defined, more collimated molecular beam.

The rotational temperature of this skimmed molecular beam was determined

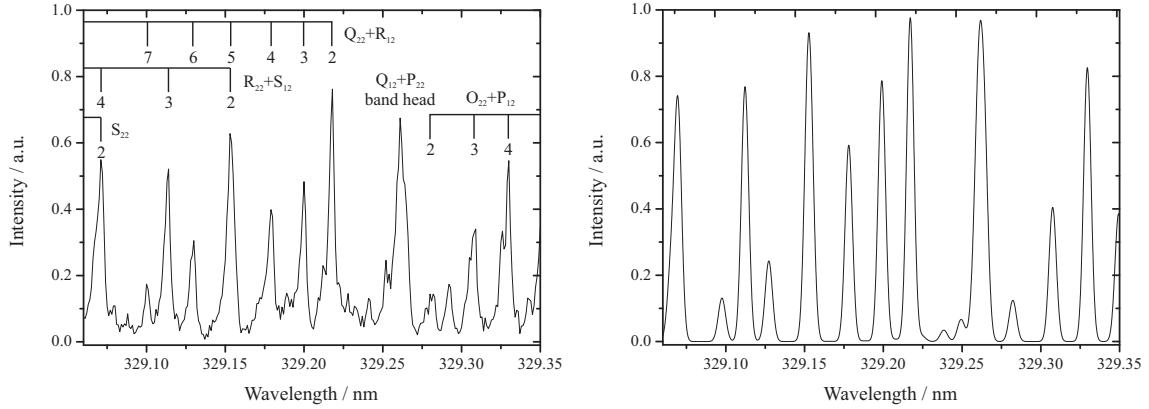


Figure 3.7: (2+1) REMPI spectrum of the E $^2\Sigma^+ \leftarrow X^2\Pi$ absorption band of NO using the skimmed molecular beam (left) and a simulation of this band using the rotational temperature determined from a Boltzmann plot (right).

from a Boltzmann plot of isolated transitions within the E $^2\Sigma^+ \leftarrow X^2\Pi$ absorption band as described previously, with 760 Torr of 5% NO (Aldrich, 99.5%) in He backing the pulsed valve. At the lower rotational temperature achieved using the skimmer, the isolated O₁₂ sub-branch transitions previously used to determine the rotational temperature of the unskimmed molecular were no longer observable. Instead, isolated transitions within the stronger Q₂₂+R₁₂ branch originating from lower J'' rotational levels were used. A Boltzmann plot of these transitions yields a rotational temperature for the skimmed molecular beam of 45 ± 5 K, significantly colder than the unskimmed beam. The (2+1) REMPI spectrum recorded in the wavelength region (329.02 – 329.35) nm is shown in figure 3.7 along with a simulation of this region assuming a rotational temperature of 45 K.

The effect of reducing this rotational temperature is illustrated by plotting the Boltzmann distribution for the rotational states of NO₂ at the two temperatures using equation (3.18). For a near-prolate C_{2v} molecule, like NO₂, J is the total rotational angular momentum quantum number and K is its projection on the C_2 axis and the energy of a rotational level is given by,

$$E_{rot} = \left(\frac{B+C}{2} \right) J(J+1) + \left(A - \frac{B+C}{2} \right) K^2. \quad (3.20)$$

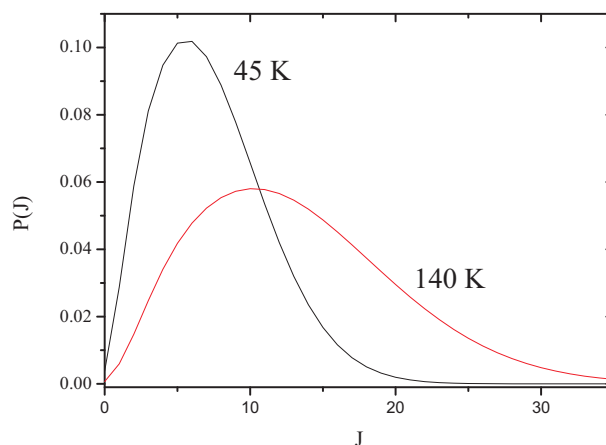


Figure 3.8: Boltzmann rotational distributions calculated for NO₂ molecules with rotational temperatures of 45 K (black) and 140 K (red).

A , B and C are the rotational constants of the molecule about the three principle axes of the molecule and K may take integer values in the range $-J \leq K \leq J$. Here B corresponds to rotation about the C_2 axis, whilst A and C correspond to rotations about axes perpendicular to the C_2 axis, with A parallel to the molecular plane and C perpendicular to the molecular plane.³⁹ The calculated Boltzmann distributions are shown in figure 3.8 and clearly show that at a rotational temperature of 45 K rotation of the parent NO₂ molecule will be significantly reduced. Vector correlations have previously been measured for the 320 nm photolysis of NO₂ using the 140 K unskimmed molecular beam⁴⁰ and the results presented in this chapter using the rotationally colder, skimmed molecular beam source will enable the effect of parent rotations on the measured vector correlations to be investigated and provide a clearer picture of the dissociation dynamics.

3.5 Probing nascent NO fragments

The skimmed molecular beam setup was used to probe the nascent NO fragments in a two-laser experiment with the first laser photolysing NO₂ at 320 nm and the second laser probing the resulting NO fragments. The REMPI scheme used to probe the photofragments was a $(1 + 1')$ ionisation *via* the A $^2\Sigma^+$ state which occurs at probe

wavelengths around 226 nm, where the prime indicates that the second ionisation photon comes from the photolysis laser and not the probe laser. This two-colour REMPI scheme was preferred over a one-colour (1 + 1) ionisation, where both photons come from the probe laser, since (1 + 1) REMPI transitions *via* the A ²Σ⁺ state are easily saturated due to the large absorption cross section of the A←X transition.⁴¹ Saturation of the probe transition will result in the angular momentum alignment dependence of the ionisation probability being lost and consequently vector correlations involving **J** will not be observed. For example, Suzuki *et al.*⁴² observed no evidence of a **v**–**J** correlation for the NO photofragments produced following NO₂ photodissociation at 355 nm when probing using a (1 + 1) REMPI scheme, whilst Baker *et al.*⁴³ have measured large values of β₀⁰(2, 2) from LIF measurements at the same dissociation wavelength. This saturation is a result of a mismatch between the A←X absorption cross section ($\sim 5 \times 10^{-16} \text{cm}^2$)⁴⁴ and the one-photon ionisation cross section of the A state ($\sim 7 \times 10^{-19} \text{cm}^2$ at 266 nm).⁴⁵ The two-colour (1 + 1') REMPI scheme allows the intensity of the probe laser to be kept low enough to ensure the A←X transition is not saturated whilst the photolysis laser power was high enough so that a sufficient signal was observed. In fact, for the experiments performed in this chapter sufficient signal was observed with the probe laser beam unfocussed and therefore the probe laser focussing lens was removed for these experiments. As a consequence of the very low probe laser intensities used for these experiments, all measured TOF profiles were unaffected by background probe-only signals. Frequent checks were made to ensure that the probe transition was not saturated and that the measured signal intensity was proportional to the probe laser power. The advantage of the (1 + 1') REMPI scheme over REMPI schemes involving two-photon absorption, for example the E←X transition used to determine the rotational temperatures, is that the number of the bipolar moments contributing to the observed signal is significantly reduced making the analysis simpler.

Saturating the photolysis step will also affect the measured vector correlations since the approximation that the absorption probability is proportional to $|\boldsymbol{\mu} \cdot \boldsymbol{\epsilon}_{\text{phot}}|^2$

will no longer be valid. Additionally, the data analysis assumes that the ionisation step of the probe REMPI scheme is completely isotropic which is often achieved by ensuring the laser power is high enough to saturate this step. In this case however, the photolysis laser both provides the photon to ionise NO molecules in their A state and dissociate the NO₂ molecules. The cross section for NO₂ absorption at 320 nm ($2.4 \times 10^{-19} \text{ cm}^2$)⁴⁶ is of a similar magnitude to the ionisation probability and it is therefore likely that saturating the ionisation step will also lead to saturation of the dissociation step. Therefore, for all experiments the photolysis laser power was kept low enough so that neither step was saturated and the measured ion intensity was proportional to the square of the photolysis laser power. It has been shown that ionisation of the A $^2\Sigma^+$ ($v = 0$) state is relatively independent of the angular momentum projection, M_J ,⁴⁷ and therefore the assumption that the ionisation probability is isotropic is valid even though the ionisation is not saturated.

In addition to the saturation of transitions, high laser powers may also cause additional unwanted *space charge* effects. This is when a sufficiently high density of ions is created such that Coulombic forces between ions are large enough to cause additional broadening of the TOF profiles which is not due to the initial velocity distribution of the photofragments. It was therefore essential to control and regularly check the power of both the probe and photolysis lasers to ensure that they were at powers where saturation and space charge effects were not affecting the measured profiles. Additionally, checks were made that varying the power of either the photolysis or probe laser by small amounts did not affect the measured vector correlations.

A (1 + 1') REMPI spectrum in the wavelength region (224.87 – 225.12) nm of nascent NO photofragments produced following dissociation of NO₂ at 320 nm is shown in figure 3.9 alongside a spectral simulation of this region.³⁵ Since $\Lambda = 0$ for the A state and all NO photofragments probed in this wavelength region are highly rotationally excited, both states will be described by Hund's case (b). The arrow on the spectrum indicates the specific isolated rotational transition which was chosen

to determine the bipolar moments of the photofragments; the $Q_{11} + P_{21}(N = 30)$ transition. This transition was chosen since it was isolated, intense and probed NO fragments which were sufficiently rotationally excited for the semi-classical description of the bipolar moments to be appropriate. Additionally, probing a high- N transition means that NO impurities in the molecular beam will not affect the observed signals since the thermal population at the molecular beam temperature of 45 K is negligible.

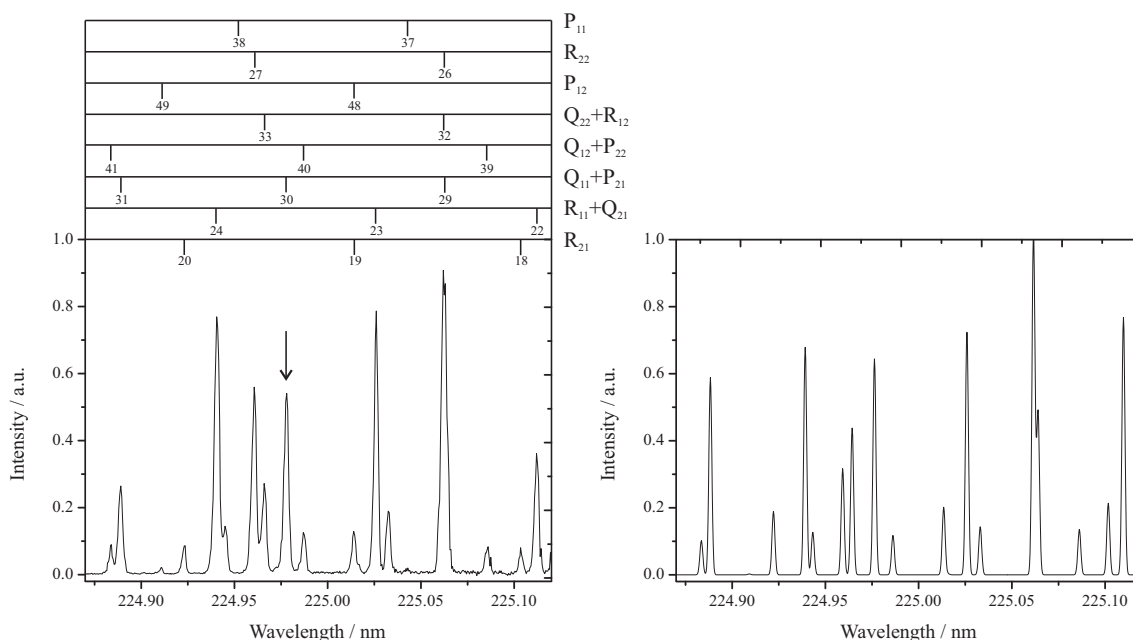


Figure 3.9: $(1 + 1')$ REMPI spectrum of the $A \ ^2\Sigma^+ \leftarrow X \ ^2\Pi$ absorption band of NO probing nascent NO photofragments produced following dissociation of NO₂ at 320 nm (left) and a simulation of this band using a best-fit rotational temperature of 1400 K (right). The arrow indicates the specific isolated rotational transition which was chosen to determine the bipolar moments of the photofragments.

The simulation was generated using literature values for the spectroscopic constants,^{35,36} a Doppler width estimated from the kinetic energy release of the $N = 30$ fragments and a best-fit rotational temperature of 1400 K. The rotational distribution of the nascent photofragments will clearly not be a simple thermal Boltzmann distribution, as is demonstrated by the significant deviations of the experimental data from the simulation, but the simulation is good enough that the transitions

present on the experimental spectrum can be confidently assigned. The closest study of NO rotational distributions to the work described in this chapter is that of Zacharias *et al.*¹⁴ who measured the rotational distribution of NO photofragments following the photolysis of NO₂ at 337 nm. They found a bimodal rotational distribution of NO with low- N and high- N photofragments best described by rotational temperatures of 65 K and 1600 K respectively. For the high- N photofragments probed in this work, the best fit rotational temperature of 1400 K is in qualitative agreement with the observations of Zacharias *et al.*.

3.6 Results

TOF profiles were taken for nascent NO photofragments produced following the dissociation of NO₂ at 320 nm by probing the Q₁₁ + P₂₁($N = 30$) A←X transition using the (1 + 1') REMPI scheme described in the previous section. The depolarisation factors, $h^{(k)}$, appearing in the expressions for the TOF profiles were calculated using table 3.1 and weighting the contributions of the overlapping Q₁₁ and P₂₁ transitions by their Hönl-London line-strength factors.^{17,34} The two depolarisation factors, $h^{(1)}$ and $h^{(2)}$, are therefore calculated to be -0.061 and 0.864 respectively. All profiles are shown in terms of the TOF shift which is the flight time of the NO⁺ ions relative to the predicted flight time for an ion formed with zero initial kinetic energy which is calculated to be 10.47 μ s.

In order to determine the experimental parameters required to model the core extraction and temporal width of the probe laser, TOF profiles were recorded in geometry G_1 and a sample profile and simulated fit shown in figure 3.10. Profiles taken in this geometry have a minimal dependence on the photofragment vector correlations and the good fit between the experimental and simulated profiles shows that core extraction and the temporal width of the probe laser are well accounted for in the simulation of the measured profiles. The profile in figure 3.10 shows only a slight dip in the centre and demonstrates that for the relatively slow (~ 1120 ms⁻¹)

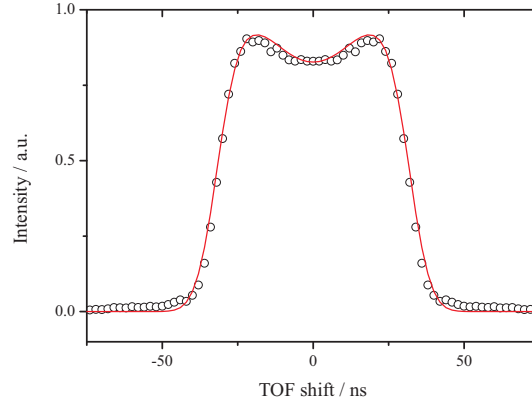


Figure 3.10: Sample experimental (open circles) and simulated (solid line) TOF profile taken in geometry G_1 used to optimise the functions accounting for the temporal width of the probe laser and core extraction.

NO photofragments probed in this work, core extraction has only a small effect.

Table 3.3: The measured values of the all bipolar moments for the NO $^2\Pi_{1/2}(N = 30, v = 0)$ photofragments produced following the photodissociation of NO₂ at 320 nm.

Bipolar moment	Vector correlation	Value
$\beta_0^2(2, 0)$	$\boldsymbol{\mu} - \mathbf{v}$	0.69 ± 0.03
$\beta_0^2(0, 2)$	$\boldsymbol{\mu} - \mathbf{J}$	-0.39 ± 0.04
$\beta_0^0(2, 2)$	$\mathbf{v} - \mathbf{J}$	-0.39 ± 0.05
$\beta_0^2(2, 2)$	$\boldsymbol{\mu} - \mathbf{v} - \mathbf{J}$	0.16 ± 0.05
$\beta_0^2(4, 2)$	$\boldsymbol{\mu} - \mathbf{v} - \mathbf{J}$	-0.25 ± 0.05
$\beta_0^2(2, 1)$	$\boldsymbol{\mu} - \mathbf{v} - \mathbf{J}$ orientation	0.3 ± 0.05

The $\beta_0^2(0, 2)$ parameter was calculated from the ratio, R , of the integrated areas of profiles taken in geometry pair G_2 . Sample profiles taken in these geometries are shown in figure 3.11 and using equation (3.11) the $\beta_0^2(0, 2)$ parameter is determined to be -0.39 ± 0.04 . All other alignment moments were determined from best-fit simulations to the sum and difference of profiles taken in the geometry pairs described in section 3.2.2. Sample sum and difference profiles are shown in figures 3.12 – 3.14 together with best-fit simulations calculated using the equations given in section 3.2.2,

following correction for core extraction and the temporal width of the probe laser determined from the profile taken in geometry G_1 . The difference profile and best-fit simulation used to extract the orientation bipolar moment, $\beta_0^2(2,1)$, is shown in figure 3.15. The measured values of all the bipolar moments are given in table 3.3.

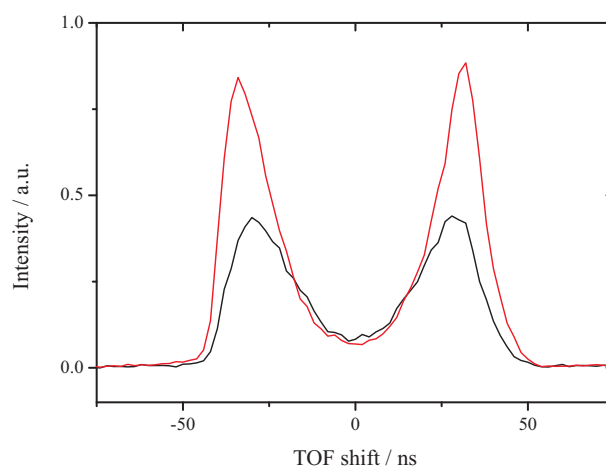


Figure 3.11: Experimental TOF profiles taken in geometry pair G_2 with the photolysis laser horizontally polarised and the probe laser switched between horizontally polarised (black) and vertically polarised (red) used to calculate the $\beta_0^2(0,2)$ parameter.

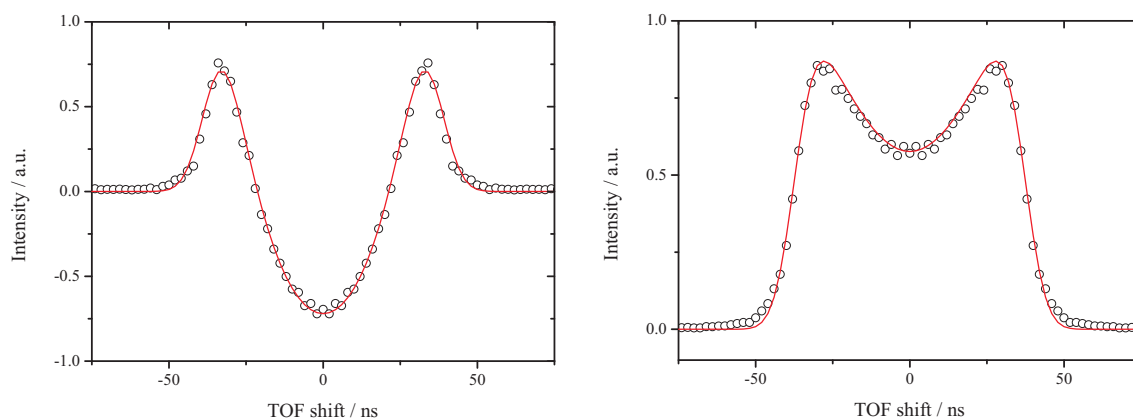


Figure 3.12: Sample experimental (open circles) and simulated (solid line) sum (right) and difference (left) profiles used to extract the $\beta_0^2(2,0)$ parameter.

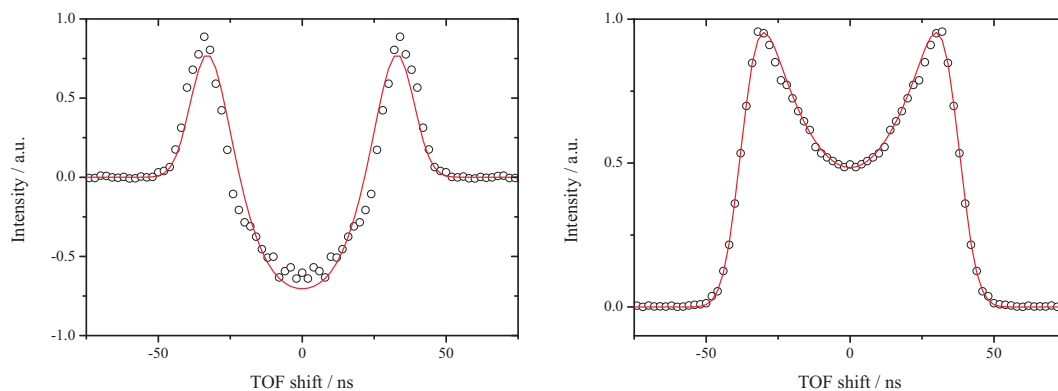


Figure 3.13: Sample experimental (open circles) and simulated (solid line) sum (right) and difference (left) profiles used to extract the $\beta_0^0(2,2)$ parameter.

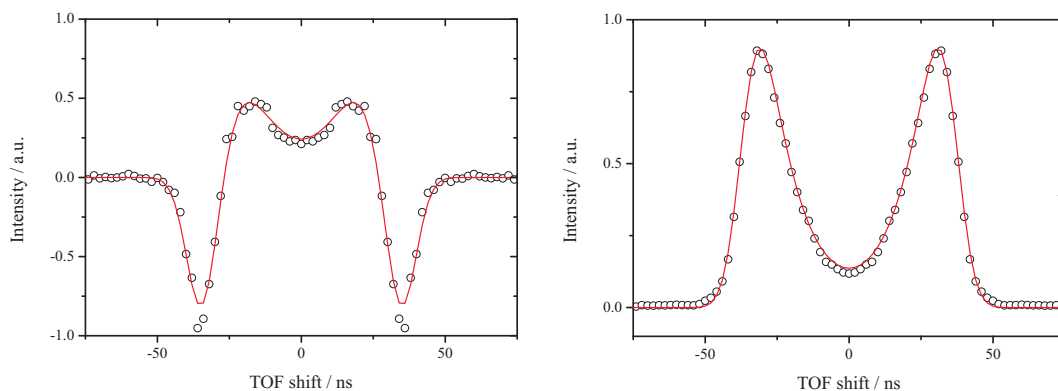


Figure 3.14: Sample experimental (open circles) and simulated (solid line) sum (right) and difference (left) profiles used to extract $\beta_0^2(2,2)$ and $\beta_0^2(4,2)$.

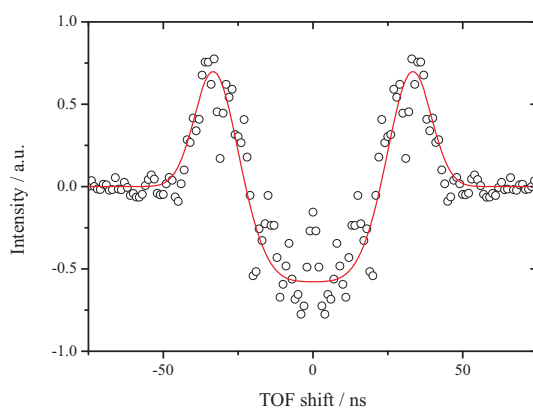


Figure 3.15: Sample experimental (open circles) and simulated (solid line) difference profiles used to extract the $\beta_0^2(2,1)$ parameter.

3.7 Discussion

3.7.1 Translational anisotropy

For the dissociation of NO₂ from its ground state equilibrium geometry with a bond angle, α , of 134.25° the translational anisotropy parameter, $\beta (= 2\beta_0^2(2, 0))$, is predicted to be 1.55 using equation (3.17). The translational anisotropy measured in this work of $\beta = 1.38 \pm 0.06$ is significantly reduced from this value and slightly higher than the value of 1.28 ± 0.06 measured by Hancock *et al.*⁴⁰ for $J = 39.5$ photofragments following dissociation at the same wavelength.

In order to explain the differences between these two results for dissociation at the same wavelength, the various possible causes of a reduction in the measured value of β must be considered. Firstly, equation (3.17) assumes the axial-recoil approximation whereby the velocity of the departing NO photofragments is assumed to be directed along the dissociating bond. For an infinitely fast dissociation of NO₂, axial recoil will occur for the production of NO molecules with zero angular momentum. If, however, rotationally excited NO molecules are produced, conservation of angular momentum dictates that there must be a transverse component to the recoil. The transverse recoil angle, φ , has been determined for a classical impulsive model to be,^{31,48,49}

$$\sin^2 \varphi = \frac{\mu_{\text{NO}} r^2 E_{\text{rot}}}{\mu_{\text{NO}_2} R_c^2 E_{\text{avl}}}, \quad (3.21)$$

where μ_{NO} and μ_{NO_2} are the reduced masses of NO and O+NO respectively, E_{avl} is the excess energy above the threshold for the specific dissociation channel, r is the internuclear NO distance and R_c is the critical distance of the departing O atom from the centre-of-mass of NO. r is assumed to be 119.34 pm⁵ whilst R_c is located in the transition state region and found experimentally to be 3.3 Å.³¹ This transverse recoil will have a large effect on the measured translational anisotropy if the excess energy is low or the rotational energy of the NO fragment is high and has been shown to effectively model the observed translational anisotropies close to the

dissociation limit.^{31,48} For the NO ²Π_{1/2}($J = 30.5, v = 0$) photofragments probed here, $E_{\text{avl}} = 1.22 \times 10^{-19}$ J and $E_{\text{rot}} = 3.23 \times 10^{-20}$ J and therefore the transverse recoil angle in this case is found to be 9.06°. This angle affects the limiting value of the β parameter and equation (3.17) is modified so that,⁴⁸

$$\beta = P_2 \left(\cos \left(\frac{\pi - \alpha}{2} + \varphi \right) \right) + P_2 \left(\cos \left(\frac{\pi - \alpha}{2} - \varphi \right) \right). \quad (3.22)$$

This reduces the predicted value of β , assuming dissociation with $\alpha = 134.25^\circ$, to 1.49 which is clearly still higher than the measured value of 1.38 ± 0.06 . This predicted limiting value of β neglects the influence of rotational motion of the parent NO₂ molecule prior to dissociation which will have a significant effect on the measured β parameter if the rotational temperature of the molecular beam is high or if the excited state lifetime is long.

There have been many measurements of the translational anisotropy close to the dissociation threshold^{31,43,48,50–52} and generally translational anisotropies measured from jet-cooled sources^{43,51} were found to be considerably larger than those from bulk, room temperature sources of NO₂.^{43,50,52} For example, Baker *et al.*⁴³ measured a β parameter of 0.81 ± 0.12 for 355 nm photolysis of a bulk sample of NO₂ at 298 K whilst for the photolysis of a jet-cooled (~ 10 K) molecular beam source at 355 nm probing the same NO fragment found that $\beta = 1.22 \pm 0.3$. The effect of the parent rotational motion will become less significant as the dissociation energy is increased due to the reduced lifetime of the excited state and higher kinetic energy release of the photofragments. It has, however, still been shown to have a small effect for photodissociation at 308 nm where Brouard *et al.* measured a β parameter of 1.22 ± 0.04 for photolysis of a sample of NO₂ at 298 K⁵³ whilst for the photolysis of a jet-cooled sample a β parameter of 1.4 ± 0.1 was measured.⁵⁴

Rotational motion of the parent molecule will reduce the observed translational anisotropy in two ways. Firstly, rotation of the parent molecule in the time period between initial photon absorption and dissociation will cause a reduction in the observed β . The reduction in β due to this effect for a diatomic molecule is

well known⁵⁵ and is given in equation (1.3). This equation may be modified for a near-prolate symmetric top by considering the long lifetime behaviour of the depolarisation function and it is found that the translational anisotropy for a near-prolate symmetric top is reduced by a factor, β_{depol} , given by,^{48,56}

$$\beta_{\text{depol}} = \frac{1 + (\omega\tau)^2}{1 + 5(\omega\tau)^2}, \quad (3.23)$$

where ω is the angular velocity of the parent molecule in rad s⁻¹ and τ is the lifetime of the excited state. Secondly, if the velocity of separation is low then the tangential velocity of the photofragments, $\mathbf{v}_t$, may not be negligible compared to the axial-recoil velocity, $\mathbf{v}_{\text{ax}}$, resulting in a tipping angle, χ , which is given by,^{48,50,52}

$$\tan \chi = \frac{\mathbf{v}_t}{\mathbf{v}_{\text{ax}}}. \quad (3.24)$$

This tipping angle will affect the measured translational anisotropy and equation (3.23) becomes,^{48,50,52}

$$\beta_{\text{depol}} = \left(\frac{P_2(\cos \chi) + (\omega\tau)^2 - 3(\omega\tau \sin \chi \cos \chi)}{1 + 5(\omega\tau)^2} \right). \quad (3.25)$$

For NO₂ molecules in a molecular beam, their angular velocity may be estimated classically as the average angular velocity for a linear molecule with a moment of inertia, I , using the equation,⁵²

$$\omega = \sqrt{\frac{\pi k_B T_{\text{rot}}}{2I}}, \quad (3.26)$$

where T_{rot} is the rotational temperature of the molecular beam and the moment of inertia, I , is approximated to be the average of the two largest moments of inertia of the NO₂ molecule. The tangential velocity is calculated using the relation, $\mathbf{v}_t = \omega r'$, where r' is the distance between the centre of mass of the NO from that of NO₂ ($r' = 0.29$ Å).⁵⁰ Using the value of $\mathbf{v}_t$ predicted from conservation of energy, the tipping angle can therefore be predicted to be 0.64° for the $J = 30.5$ NO

photofragments probed in this work. Using an upper estimate for the excited state lifetime of 100 fs¹¹ the calculated value of β_{depol} using equation (3.25) for a molecular beam temperature of 45 K is found to be 0.99 and therefore depolarisation due to parent molecular rotations is negligible for this work.

None of these causes of reduced translational anisotropy can account for the value of $\beta = 1.38 \pm 0.06$ observed in this work if dissociation occurs from the ground state equilibrium bond angle of $\alpha = 134.25^\circ$. As mentioned previously, the NO₂ molecule dissociates with an excited bending motion and therefore it is likely that the molecule will dissociate at an intermediate angle between the bond angle at which the conical intersection is accessed ($\sim 108^\circ$) and the ground state equilibrium geometry. Using equations (3.25) and (3.22) it is found that an experimental value of $\beta = 1.38 \pm 0.06$ is best fit by an average dissociating bond angle of 128° . This is in excellent agreement with the value of $\alpha = 126^\circ$ measured by Demyanenko *et al.*³¹ for dissociation at 338.9 nm. This bond angle can also be used in equations (3.25) and (3.22) to determine the predicted β parameter for the $J = 39.5$ NO fragments probed by Hancock *et al.*⁴⁰ following dissociation at 320 nm from an unskimmed, 140 K molecular beam source. The predicted value of β under these conditions is 1.31 and in excellent agreement with the value of 1.28 ± 0.06 measured in their work.

3.7.2 Angular momentum alignment

The measured values of $\beta_0^2(0, 2)$ ($\boldsymbol{\mu}-\mathbf{J}$ correlation) and $\beta_0^0(2, 2)$ ($\mathbf{v}-\mathbf{J}$ correlation) of -0.39 ± 0.04 and -0.39 ± 0.05 respectively show that the angular momentum of the NO $J = 30.5$ photofragments is aligned preferentially perpendicular to both $\mathbf{v}$ and $\boldsymbol{\mu}$, as predicted by the impulsive model. The value of $\beta_0^0(2, 2)$ measured here is in excellent agreement with the value of -0.41 ± 0.06 measured by Hancock *et al.*⁴⁰ for NO $J = 39.5$ fragments, whilst the value of $\beta_0^2(0, 2) = -0.3 \pm 0.05$ measured in their work is significantly lower than that measured here. This discrepancy is due to the influence of parent rotational motion on the measured alignment. The measured $\beta_0^2(0, 2)$ parameter will be depolarised in a similar way to the translational

anisotropy in equation (3.23) due to rotational motion of the parent molecule in the time between initial photon absorption and dissociation since it also depends on the alignment of $\boldsymbol{\mu}$ in the laboratory frame. The $\beta_0^0(2, 2)$ parameter, however, depends on the angle between $\mathbf{v}$ and $\mathbf{J}$ which are both defined after the instant of dissociation and therefore does not depend on the alignment of $\boldsymbol{\mu}$ in the laboratory frame. This means that for the dissociation of rotationally excited parent molecules the measured $\beta_0^2(0, 2)$ parameter will be reduced whilst the $\beta_0^0(2, 2)$ parameter will be unaffected as is demonstrated by the smaller value of $\beta_0^2(0, 2)$ measured by Hancock *et al.*⁴⁰ for dissociation of molecules at 140 K. In the previous section it was shown that for the 45 K skimmed molecular beam used in this work, rotational depolarisation of the measured translational anisotropy was negligible and therefore the measured value of $\beta_0^2(0, 2)$ is also expected to be unaffected by this depolarisation, resulting in the larger measured value. In this situation, the angle between $\mathbf{v}$ and $\mathbf{J}$ is now the same as the angle between $\boldsymbol{\mu}$ and $\mathbf{J}$ as is demonstrated by the identical values of $\beta_0^2(0, 2)$ and $\beta_0^0(2, 2)$.

The measured values of $\beta_0^2(0, 2)$ and $\beta_0^0(2, 2)$ are still significantly reduced from the limiting value of -0.5 predicted by a pure impulsive dissociation. This reduction in the measured angular momentum alignment may be caused by in-plane molecular rotations of the parent molecule which will cause the photofragment angular momentum vector, $\mathbf{J}$, to rotate towards the molecular plane so that it is no longer perpendicular to the plane. Even at the low rotational temperature of 45 K used in this work this will still have a significant effect on the measured angular momentum alignment. This effect may be estimated classically using a Boltzmann distribution of the in-plane rotations, J_A and J_B , for parent molecules at 45 K from which the average angle between $\mathbf{J}$ and the molecular plane is found to be 76° . This corresponds to $\beta_0^0(2, 2) = -0.41$ using the equation in table 3.2, in good agreement with the observed results. Bass *et al.*⁵⁴ have measured a limiting value of $\beta_0^0(2, 2) = -0.5 \pm 0.11$ for dissociation at 308 nm using an even colder molecular beam source, demonstrating that in the absence of parent rotation a limiting alignment will be observed.

The triple vector correlations, $\beta_0^0(2, 2)$ and $\beta_0^2(4, 2)$, may be estimated by determining the body-fixed frame angles from the vector correlations already determined using the equations given in table 3.2 and inserting them into the equation given in table II of Ref. 15. This yields values of 0.14 and -0.31 for $\beta_0^0(2, 2)$ and $\beta_0^2(4, 2)$ respectively, in good agreement with the measured values of 0.16 ± 0.05 and -0.25 ± 0.05 and therefore confirming the picture of dissociation with $\boldsymbol{\mu}$ and $\mathbf{v}$ in the same molecular plane and both preferentially perpendicular to $\mathbf{J}$.

3.7.3 Angular momentum orientation

The measure value of $\beta_0^2(2, 1) = 0.3 \pm 0.05$ is consistent with $\mathbf{J}$ oriented preferentially parallel to $\boldsymbol{\mu} \times \mathbf{v}$, as would be expected for a purely impulsive dissociation. Using the body-fixed angles of $\theta_t = 26^\circ$ and $\theta_r = 74^\circ$ implied from the alignment measurements we can calculate the limiting value of $\beta_0^2(2, 1)$ from table 3.2 to be 0.76 assuming $(\phi_r - \phi_t) = 90^\circ$. Parent molecular rotations will cause $(\phi_r - \phi_t)$ to deviate slightly from 90° but not significantly enough to account for the large deviation from the limiting value observed here. Instead, the reduced measured orientation is most likely due to the bending motion of the molecule as it dissociates. The NO₂ molecule will relax from the geometry at which the conical intersection is accessed ($\sim 108^\circ$) to the ground state equilibrium geometry (134.25°) and this bond opening motion will impart an associated torque on the NO photofragments. This torque will be oriented in an opposite direction to the impulsive torque and result in a reduced photofragment orientation. This observed $\beta_0^2(2, 1)$ orientation is slightly larger than 0.25 ± 0.04 observed by Hancock *et al.*⁴⁰ for dissociation at 320 nm, 0.22 ± 0.04 measured by Brouard *et al.*⁵³ at 308 nm and ~ 0.2 measured by Nesterov *et al.*²⁴ at 355 nm. These smaller measured orientations are most likely due to rotational depolarisation since, like the $\beta_0^2(0, 2)$ parameter, the $\beta_0^2(2, 1)$ parameter also depends on the laboratory frame alignment of $\boldsymbol{\mu}$ and the measurements at 320 nm and 308 nm were both taken using higher rotational temperature samples. The rotational temperature of the parent molecules used by Nesterov *et al.*²⁴ is not mentioned but

the longer excited state lifetime at 355 nm will make rotational depolarisation more significant even for a rotationally cooled beam.

3.8 Conclusions

The work presented in this chapter has investigated the stereodynamics of the photodissociation of NO₂ at 320 nm. The measured vector correlations are found to be consistent with an impulsive model for the dissociation with μ and $\mathbf{v}$ in the same molecular plane and both preferentially perpendicular to $\mathbf{J}$, whilst angular momentum orientation measurements provide evidence for an additional torque due to the O–N–O bond opening as it dissociates. The results were taken with a molecular beam rotational temperature of 45 K and have been compared with previous results taken with a rotationally hotter molecular beam source.⁴⁰ Distinguishable differences between the two sets of results have been observed and these have been found to be due to rotational motion of the parent NO₂ molecules. The effect of parent molecular rotations on the measured vector correlations has been quantified and used to provide a clear picture of the dissociation mechanism.

Whilst this work adds to the general understanding of NO₂ photolysis and the effect of parent molecular rotations on the observed dissociation dynamics, the main aim of this work was to test the reliability of the experimental setup on a well-known system following the incorporation of a skimmer. The motivation for incorporating the skimmer into the experimental setup and cooling the molecular beam was to investigate the role of parent molecular rotations in the photolysis of ozone in the Hartley band.^{40,57,58} Angular momentum alignment measurements for dissociation of ozone at 270 nm within the Hartley band have shown the odd J O₂ $^1\Delta_g$ states to be significantly depolarised from the even J states. Odd and even J states of O₂ $^1\Delta_g$ are associated with different Λ -doublets and it is thought that the reduced alignment of odd J states is due to rotations in the molecular plane favouring the $^1\Delta_g^-$ Λ -doublet, which is associated with these odd J states.⁵⁷ Unfortunately, the loss of molecular beam density at the centre of the source region of the TOF spectrometer due to the

incorporation of a skimmer into the experimental setup resulted in O₂ ¹Δ_g signals being too low to accurately measure the angular momentum alignment and these experiments were not possible. All other experiments described in this thesis were performed using an unskimmed molecular beam in order to maximise the molecular beam density in the source region and therefore the observed photofragment ion signals.

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Chapter 4

Atomic polarisation in the UV photodissociation of Cl_2

This chapter describes measurements of photofragment angular momentum orientation and alignment following the dissociation of Cl_2 in the wavelength region (320 – 350) nm. The angular momentum polarisation of atomic photofragments is described in terms of a polarisation parameter formalism and this chapter demonstrates how these parameters, as well as the translational anisotropy, may be extracted from TOF profiles taken in a series of different geometries. It is shown how both the translational anisotropy and angular momentum polarisation of the atomic photofragments may be interpreted and used to elucidate the dissociation mechanism. The results presented in this chapter were taken in partnership with Tom Sharples, whilst the data analysis has been performed independently.

4.1 Introduction

The UV photodissociation of Cl_2 has been the subject of many investigations due to chlorine being more experimentally accessible than hydrogen or fluorine whilst still being relatively simple enough to allow detailed theoretical investigations thus making it an ideal case for comparison between experiment and theory.¹ The first UV absorption band of Cl_2 is a continuous, bell-shaped distribution in the wavelength

region (250 – 450) nm peaking at 335 nm and is shown in figure 4.1. Following the absorption of UV in this band the Cl₂ molecule may dissociate *via* two main channels producing either ground-state Cl (²P_{3/2}) or electronically excited Cl* (²P_{1/2}) atoms,



Early studies of the branching ratio for these two channels^{2–5} have found the dominant dissociation channel to be that producing two ground-state Cl atoms, with Matsumi *et al.*⁵ measuring a ratio of ground to excited state atoms of 100 : 1 at 351 nm. The wavelength dependence of this branching ratio has been measured^{6–8} and is found to be very sensitive to photolysis wavelength, with the ratio of ground to excited state atoms found to be 0.003 ± 0.01 at 350 nm rising to 0.75 ± 0.03 at 440 nm.⁸

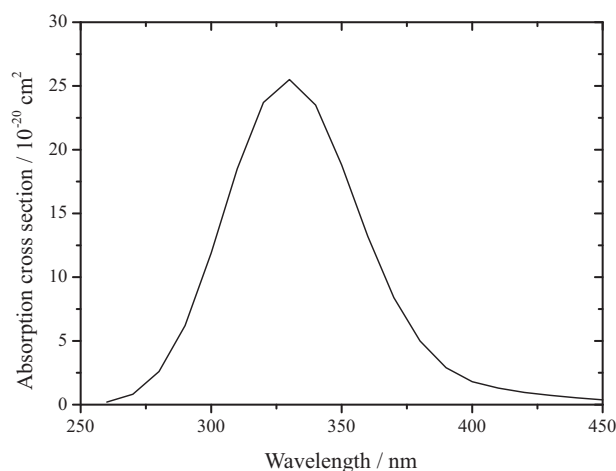


Figure 4.1: Absorption cross section for the first UV absorption band of Cl₂. Data taken from Ref. 9.

Dynamics studies have revealed the potential energy surfaces involved in this dissociation process and these are illustrated in figure 4.2. The strong spin-orbit interaction in atomic chlorine mandates a Hund’s case (c) description of Cl₂ where

the spin-orbit interaction between $\mathbf{L}$ and $\mathbf{S}$ is now stronger than the electrostatic coupling to the internuclear axis. In this case, $\mathbf{L}$ and $\mathbf{S}$ couple to form a resultant angular momentum, $\mathbf{J}_\alpha$, which is subsequently coupled to the internuclear axis with a component, Ω . This projection, Ω , then couples with the nuclear rotation, $\mathbf{N}$, to form a resultant total angular momentum, $\mathbf{J}$.¹⁰ The projections of $\mathbf{L}$ and $\mathbf{S}$ on the internuclear axis, Λ and Σ respectively, are no longer defined and states are labeled according to their value of Ω . In this work the molecular states will be described using a mixed case (a)/(c) notation as employed previously by Asano and Yabushita,¹¹ where molecular states are given their usual case (a) term symbol with the case (c) term symbol given as a subscript. For example, the ground state is denoted $X^1\Sigma_{0g}^+$, where 0_g^+ is the case (c) term symbol and $^1\Sigma_g^+$ is the associated Hund's case (a) molecular state.

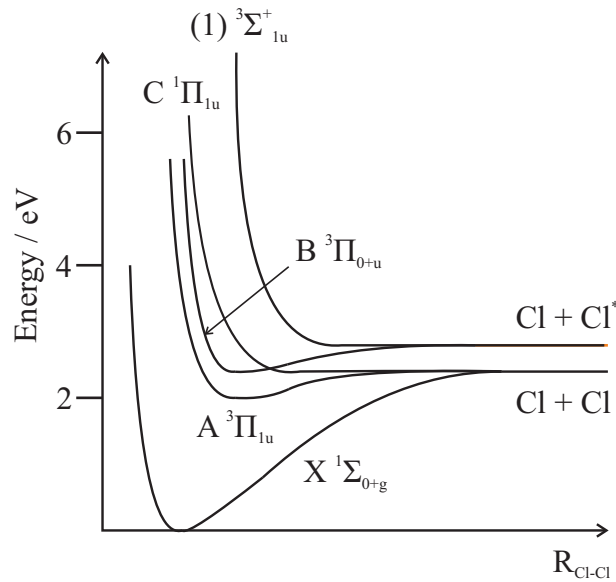


Figure 4.2: Illustration of potential energy curves for the molecular states of Cl₂ which are important for dissociation within the first absorption band, adapted from Ref. 12.

Translational anisotropy measurements for the (Cl + Cl) dissociation channel have shown it to be due to a perpendicular transition²⁻⁸ which, within the case (c) notation, corresponds to a $\Delta\Omega = \pm 1$ transition. A correlation diagram may be

constructed between the molecular states in both Hund's case (a) and (c) and the electronic states of separated Cl atoms using the adiabatic correlation rules of Mulliken,¹³ whereby the non-crossing rule applies to wavefunctions with the same value of Ω and therefore the energy ordering of Hund's case (c) molecular states at short range will be maintained until dissociation. This has been presented previously^{4,6,14} and it is clear that dissociation to the (Cl + Cl) channel occurs *via* a perpendicular transition to the dissociative C $^1\Pi_{1u}$ state which correlates adiabatically to the (Cl + Cl) dissociation limit. Translational anisotropy measurements of the Cl* photofragment⁶⁻⁸ have been found to depend upon the photolysis wavelength, with a limiting value of $\beta = +2 \pm 0.05$ measured at 400 nm indicating a parallel transition ($\Delta\Omega = 0$) which decreases as the dissociation wavelength is reduced to a value of -0.64 ± 0.05 at 310 nm indicating an increasingly perpendicular transition. At long wavelengths, the production of Cl* atoms is thought to result from a parallel transition to the B $^3\Pi_{0+u}$ state which correlates adiabatically to the (Cl + Cl*) dissociation limit.⁶⁻⁸ This transition is spin forbidden but is partially allowed due to spin-orbit mixing between the ground X $^1\Sigma_{0g}^+$ state and excited $^3\Sigma_g^-$ states.¹¹ As the dissociation wavelength is decreased, the increasing contribution from a perpendicular transition resulting in Cl* production is thought to arise from a perpendicular excitation to the C $^1\Pi_{1u}$ state followed by non-adiabatic coupling with the excited (1) $^3\Sigma_{1u}^+$ state which correlates adiabatically with the (Cl + Cl*) limit.^{11,14}

There have been many previous studies of the electronic alignment of the Cl atoms produced following UV dissociation, the first of which was by Wang *et al.*¹⁵ using REMPI-TOF with their measured Cl alignment being found to show a preference for $M_J = \pm 1/2$ ^{16,17} as would be expected for adiabatic dissociation along the C $^1\Pi_{1u}$ state. More detailed studies of the photofragment alignment have revealed that the dissociation does not occur adiabatically along the C $^1\Pi_{1u}$ state and, in fact, non-adiabatic transitions to the A $^3\Pi_{1u}$ state in the long range region of the potentials play a significant role in the dissociation mechanism.^{8,18-22} Bracker *et al.*¹⁹ measured the Cl atomic alignment using ion imaging, reporting the angular mo-

mentum polarisation in terms of a set of alignment anisotropy parameters¹⁸ which are normalised functions of the quantum mechanical dynamical functions derived by Siebbeles *et al.*²³ which they extracted from ion imaging data. Rakitzis *et al.*²⁰ showed how the atomic alignment of Cl may be interpreted in terms of an alternative set of molecular-frame polarisation parameters²⁴ which they extracted from REMPI-TOF profiles. This polarisation parameter formalism will be used in this chapter to interpret the alignment of Cl following dissociation in the wavelength region (320 – 350) nm. There have been previous measurements of the Cl photofragment alignment following dissociation at 308 nm,²² 320 nm,²⁰ and 355 nm^{18,19,21} and, whilst all these studies are in general agreement that non-adiabatic transitions to the A ³Π_{1u} state play an important role in the dissociation process, there are significant variations in the extent of these non-adiabatic transitions implied by the angular momentum alignment measurements at different photolysis wavelengths and the two different studies at 355 nm. This is in contradiction with theoretical calculations^{11,12,25,26} which predict the non-adiabatic transitions to be relatively constant over this wavelength range. The aim of this work is therefore to determine whether these experimental variations are a real effect or simply a consequence of comparing experimental data taken using a variety of experimental techniques in different laboratories. The angular momentum of the electronically excited, Cl* photofragment cannot be aligned, as $|M_J| = 1/2$ but it can, however, be oriented. Interference between the two possible dissociation channels of different symmetry has been shown to result in a coherent orientation of the Cl* angular momentum orientation in a manner analogous to a variant of the Young's double-slit experiment, where two slits transmitting light of perpendicular polarisations will result in a polarisation fringe pattern instead of the usual intensity fringe pattern.²⁰ This effect may also be interpreted in terms of the molecular-frame polarisation parameters and has been measured previously by Zare and co-workers^{14,20,27,28} for a series of wavelengths in the range (270 – 400) nm and will also be determined in this chapter. The exact values and interpretation of these polarisation parameters will be discussed in de-

tail later, whilst the next section will describe the derivation of these polarisation parameters and how they may be determined from TOF profiles.

As mentioned previously, the photodissociation of Cl₂ provides an excellent system for comparison between experiment and theory and consequently there have been several different theoretical studies of this process. Whilst there have been several high-level studies to determine the potential energy curves of Cl₂,^{11,29–32} there have relatively few theoretical studies of the photodissociation dynamics. Asano and Yabushita^{11,12} used their set of calculated adiabatic potentials to predict the non-adiabatic transitions involved in the dissociation process assuming radial Rosen-Zener-Demkov (RDZ) type transitions. This allowed them to semi-classically predict some of the dynamical parameters and will be discussed in more detail later. Most significantly for the work described in this chapter, Johnsen *et al.*²⁶ have determined all of the dynamical parameters for the dissociation of Cl₂ in a fully quantum mechanical study. This is an extension of the work by Balint-Kurti *et al.*³³ who have outlined the direct link between the measured angular momentum polarisation parameters and the fully quantum-mechanical photofragment scattering, *T*-matrix formalism which they used to determine the polarisation parameters for the dissociation of halides.^{33–35} The *T*-matrix elements contain all the dynamical information relating to the dissociation process of interest, with each matrix element corresponding to a particular dissociation channel and is, in general, a complex number consisting of an amplitude and a phase factor. The *T*-matrix elements of the dissociation process may be calculated using a time-dependent quantum mechanical wavepacket treatment using *ab initio* potential energy curves, spinorbit couplings, and dipole moments. Kokh *et al.*^{30,31} derived a set of adiabatic potential energy surfaces and associated transition dipole moments using the multi-reference single- and double-excitation configuration interaction (MRD-CI) method including spinorbit coupling, which quantitatively described the experimental absorption spectrum. To determine the *T*-matrix elements for Cl₂ photodissociation, an initial wavepacket is generated by multiplying the ground state wavefunction by appropri-

ate transition dipole moment and projecting it onto these excited potentials. This wavepacket is subsequently allowed to propagate quantum mechanically along these excited potential energy surfaces and sampled at regular time-steps to determine the photofragment $\mathbf{T}$ -matrix elements.²⁶ These $\mathbf{T}$ -matrix are directly related to the $f_K(q, q')$ dynamical functions^{23,33} which are subsequently used to construct the experimentally observable polarisation parameters *via* a set of simple relationships.^{1,36} The angular momentum polarisation measurements presented in this chapter will be compared to the quantum mechanical calculations of Johnsen *et al.*²⁶ and has been presented in a recent publication.²⁵

4.2 Measuring atomic orbital polarisation

4.2.1 Relating TOF profiles to polarisation parameters

As mentioned in the introduction, the molecular-frame polarisation parameter formalism developed by Rakitzis and Zare²⁴ will be used in this thesis to describe the atomic angular momentum alignment. Within this formalism, the spatial distribution, $D(\theta, \phi)$, of the photofragment angular momentum, $\mathbf{J}$, is expanded in terms of the modified spherical harmonics as in equation (1.4), where the coefficients of this expansion are the polarisation parameters, $A_q^{(k)}(J)$, defined in chapter 1. These parameters may be used to describe the photofragment angular momentum in the molecular frame, where the polar angles, (θ, ϕ) , appearing in equation (1.4) will be relative to a z -axis lying along the the photofragment velocity vector, $\mathbf{v}$, and an x -axis lying in the plane of $\mathbf{v}$ and the electric vector of the photolysis light, $\boldsymbol{\epsilon}_{\text{phot}}$.²⁴ This will only describe the photofragment angular momentum for a fixed angle, θ_ϵ , between $\boldsymbol{\epsilon}_{\text{phot}}$ and $\mathbf{v}$ since $A_q^{(k)}(J)$ will in general depend on θ_ϵ . In order to describe the photofragment angular momentum for an arbitrary value of θ_ϵ , the distribution must be split up into contributions from pure parallel or perpendicular transitions, which will not depend on θ_ϵ , with the complete angular momentum distribution built up from incoherent and coherent contributions from these transitions.

This is achieved by defined a set of molecular-frame polarisation parameters, $a_q^{(k)}(p)$, where p denotes the symmetry of the transition excited; parallel ($\parallel$), perpendicular ($\perp$) or mixed ($\parallel, \perp$).²⁴ For a pure parallel transition, there is cylindrical symmetry about the internuclear axis so that only cylindrically symmetric parameters may be non-zero ($q = 0$) and, since there is no net change of the total angular momentum projection onto the bond axis, there must be no net orientation and therefore parameters with odd- k must be zero. The distribution, $D_{\parallel}(\theta)$, of photofragment angular momentum resulting from a pure parallel transition is therefore given by,²⁴

$$D_{\parallel}(\theta) = \sum_{\text{even } k}^{2J} a_0^{(k)}(\parallel) C_0^k(\theta). \quad (4.3)$$

For a pure perpendicular transition, the cylindrical symmetry is broken and q may now be non-zero and the distribution, $D_{\perp}(\theta, \phi)$, of photofragment angular momentum resulting from a pure perpendicular transition is given by,²⁴

$$D_{\perp}(\theta, \phi) = \sum_{k=0}^{2J} \sum_{q=-k}^k a_q^{(k)}(\perp) C_q^k(\theta, \phi). \quad (4.4)$$

In this sum, parameters where $|q|$ is odd are now zero due to the reflection symmetry of the perpendicular transition. If a mixed transition occurs, the total photofragment angular momentum distribution, $D_{\parallel, \perp}(\theta, \phi)$, will consist of incoherent contributions from pure parallel and perpendicular transitions as well as coherent interference between the two transitions. The breaking of symmetry for a mixed parallel/perpendicular transition allows the existence of extra parameters and it has been shown that the interference between one-photon perpendicular and parallel transitions is completely described by parameters with $|q| = 1$.^{23,37} The relative weighting for the different contributions will be given by the β parameter for the transition, assuming that the only cause for deviations of β from its limiting values of $+2$ or -1 is due to excitations to surfaces of different symmetries. $D_{\parallel, \perp}(\theta, \phi)$ is

therefore given by,

$$D_{\parallel,\perp}(\theta, \phi) = \left((1 + \beta) \cos^2 \theta_\epsilon D_{\parallel}(\theta) + (1 - \beta/2) \sin^2 \theta_\epsilon D_{\perp}(\theta, \phi) \right. \\ \left. + 2\sqrt{(1 + \beta)(1 - \beta/2)} \sin \theta_\epsilon \cos \theta_\epsilon \sum_{k=0}^{2J} a_1^{(k)}(\parallel, \perp) C_1^k(\theta, \phi) \right) / \quad (4.5) \\ (1 + \beta P_2(\cos \theta_\epsilon)).$$

By comparing this equation with equation (1.4) the relation between the molecular-frame, $A_q^{(k)}(J)$, polarisation parameters and the $a_q^{(k)}(p)$ parameters may be derived.

The REMPI detection probability, I_{det} , for polarised light in terms of the molecular-frame polarisation parameters has been derived by Kummel, Sitz and Zare,³⁸

$$I_{\text{det}} = \sum_{k=0}^{2n} \sum_{q=-k}^k P_q^{(k)} A_q^{(k)}(J) C_q^k(\theta, \phi), \quad (4.6)$$

where n is number of probe photons required to reach the resonant state in a $(n + m)$ REMPI process and θ and ϕ are the polar angles describing the probe laser electric vector, ϵ_{probe} , relative to $\mathbf{v}$. The $P_q^{(k)}$ factors are line-strength factors which are relatively complicated functions depending on the initial and final states involved in the resonant detection step and have been derived for linear, circular and elliptically polarised probe light^{38,39} by considering the coupling between all the possible virtual intermediate states for a $(2 + 1)$ REMPI detection scheme.

By expressing the $A_q^{(k)}(J)$ parameters appearing in equation (4.6) in terms of the $a_q^{(k)}(p)$ parameters as described earlier, a molecular-frame detection probability in terms of these parameters may be determined. This detection probability is for photofragments with a fixed scattering angle, θ_ϵ , relative to unpolarised photofragments with the same angular distribution.⁴⁰ This should then be renormalised so that it is relative to unpolarised photofragments with an isotropic scattering distribution by multiplying by the scattering angular distribution, $I(\theta_\epsilon)$, which, for a one-photon dissociation using linearly polarised light from an isotropic ensemble of molecules within the axial-recoil approximation, is given by, $(1 + \beta P_2(\cos \theta_\epsilon))$.⁴¹ For

a one-photon dissociation with linear polarised light, the only interference parameters, $a_1^{(k)}(\parallel, \perp)$, appearing in equation (4.5) which may be observed are $\text{Re}[a_1^{(k)}(\parallel, \perp)]$ with even k and $\text{Im}[a_1^{(k)}(\parallel, \perp)]$ with odd k .²⁴ The resulting molecular-frame detection probability, I_{det} , for the detection of $J = 3/2$ Cl atoms produced following the one-photon dissociation of Cl₂ with linear polarised light in terms of the $a_q^{(k)}(p)$ parameters is therefore given by,

$$\begin{aligned}
 I_{\text{det}} = & 1 + \beta P_2(\cos \theta_\epsilon) \\
 & + 2s_1 \sin \theta_\epsilon \cos \theta_\epsilon \text{Im}[a_1^{(1)}(\parallel, \perp)] C_1^1(\theta) \sin \phi \\
 & + s_2(1 + \beta) \cos^2 \theta_\epsilon a_0^{(2)}(\parallel) C_0^2(\theta) \\
 & + s_2(1 - \beta/2) \sin^2 \theta_\epsilon \left(a_0^{(2)}(\perp) C_0^2(\theta) + 2a_2^{(2)}(\perp) C_2^2(\theta) \cos 2\phi \right) \\
 & + 2s_2 \sin \theta_\epsilon \cos \theta_\epsilon \text{Re}[a_1^{(2)}(\parallel, \perp)] C_1^2(\theta) \cos \phi \\
 & + 2s_3 \sin \theta_\epsilon \cos \theta_\epsilon \text{Im}[a_1^{(3)}(\parallel, \perp)] C_1^3(\theta) \sin \phi.
 \end{aligned} \tag{4.7}$$

Note that since $a_2^{(2)}(\perp)$ is real, $a_{+2}^{(2)}(\perp) = a_{-2}^{(2)}(\perp)$. Here the convention of Rakitzis and Zare²⁴ has been used and the $\text{Im}[a_1^{(k)}(\parallel, \perp)]$ and $\text{Re}[a_1^{(k)}(\parallel, \perp)]$ parameters have been defined to include the $\sqrt{(1 + \beta)(1 - \beta/2)}$ weighting term.

The s_k parameters appearing in equation (4.7) are equal to relative ratio of the line-strength factors derived by Kummel, Sitz and Zare, $P_0^{(k)}/P_0^{(0)}$.^{38,39} Mo and Suzuki⁴² have shown that for the state multipole moments, $\rho_0^{(k)}$, of the density matrix⁴³ this ratio of line-strength factors, P_k , for a two-photon probe transition from an initial state, J_i , to a final state, J_f , is given by the simple expression,

$$P_k = 5\sqrt{2k+1}\sqrt{2J_i+1}(-1)^{J_i+J_f} \begin{pmatrix} 2 & 2 & k \\ 2s & -2s & 0 \end{pmatrix} \begin{Bmatrix} J_i & J_i & k \\ 2 & 2 & J_f \end{Bmatrix}, \tag{4.8}$$

where the term in large curly brackets is a Wigner-6J coefficient,⁴⁴ $s = 0$ for linear polarised light, $+1$ for left circular polarised light and -1 for right circular polarised light.⁴⁵ This equation applies to all allowed two-photon transitions if circular polarised light is used but if linear polarised light is used, this expression is only

applicable when $J_i \neq J_f$ and the full summation over all the possible virtual intermediate states is required to determine P_k for a Q-branch transition.⁴² The multipole moments are easily converted into the polarisation parameters used in this work and the required line-strength factors are therefore given by,^{44,46}

$$s_k = \frac{c(k) \langle J || J^{(k)} || J \rangle}{[J(J+1)]^{k/2} \sqrt{2k+1}} P_k, \quad (4.9)$$

where all the terms appearing in the expression are as defined in equation (1.8).

If the atom has a non-zero nuclear spin angular momentum, $\mathbf{I}$, then hyperfine coupling between $\mathbf{J}$ and $\mathbf{I}$ will cause a depolarisation of the observed angular momentum distribution. If the photodissociation causes an initially aligned distribution of $\mathbf{J}$ which is described by a set of polarisation parameters, $A_q^{(k)}(J, t=0)$, then the subsequent coupling of $\mathbf{J}$ and $\mathbf{I}$ will form a resultant angular momentum, $\mathbf{F}$, which, according to the vector model, will cause $\mathbf{J}$ to precess about $\mathbf{F}$. This will result in a time dependent polarisation of $\mathbf{J}$ and the distribution of $\mathbf{J}$ at a time, t , following the initial photodissociation process will be described by a set of time-dependent polarisation parameters, $A_q^{(k)}(J, t)$, given by,⁴⁴

$$A_q^{(k)}(J, t) = G^{(k)}(t) A_q^{(k)}(J, t=0). \quad (4.10)$$

$G^{(k)}(t)$ is a depolarisation factor which oscillates with a time period which is proportional to the energy splittings between quantum states with different $\mathbf{F}$. For Cl these energy splittings are small (205 MHz for ³⁵Cl)⁴⁷ and therefore the oscillations of $G^{(k)}(t)$ will be rapid compared to the temporal width of the probe laser (~ 10 ns) so that it may be given by its time-averaged value, $\langle G^{(k)}(t) \rangle_{\text{av}}$, which is given by,⁴⁴

$$\langle G^{(k)}(t) \rangle_{\text{av}} = \sum_F \frac{(2F+1)^2}{2I+1} \left\{ \begin{matrix} F & F & k \\ J & J & I \end{matrix} \right\}^2. \quad (4.11)$$

The line-strength factors required in this chapter may therefore be simply calculated using equation (4.9) with subsequent correction for the nuclear spin of Cl atoms

of $I = 3/2$. For the ground state Cl atoms, ionisation was *via* the $^2S_{1/2} \leftarrow \leftarrow ^2P_{3/2}$ transition at 234.640 nm.⁴⁸ For this fragment only linear polarised probe light was used so that $s_1 = s_3 = 0$ and s_2 is calculated to be -0.3375 . For the electronically excited Cl* atoms, ionisation was *via* the $^2P_{3/2} \leftarrow \leftarrow ^2P_{1/2}$ transition at 236.527 nm.⁴⁸ For this fragment only polarisation parameters where $k \leq 1$ may be non-zero and for left circular polarised probe light the line-strength factor, s_1 , is calculated to be -0.6495 .

Finally, the molecular-frame detection probability, I_{det} , must be transformed into the laboratory frame to compare with the observed experimental profiles. This transformation is achieved by defining three sets of laboratory-frame angles, $(\theta_D, 0)$, (Θ, Φ) and (γ, χ) which define ϵ_{phot} , ϵ_{probe} and $\mathbf{v}$ respectively relative to the laboratory z -axis which is defined to be the TOF axis. The molecular frame angles θ_ϵ , θ and ϕ in equation (4.7) are related to the laboratory frame angles using the spherical harmonic addition theorem⁴⁴ together with equations (20–22) of Ref. 24. These relations are given by,^{40,49}

$$\cos \theta_\epsilon = \cos \gamma \cos \theta_D + \sin \gamma \sin \theta_D \cos \chi, \quad (4.12)$$

$$\cos \theta = \cos \gamma \cos \Theta + \sin \gamma \sin \Theta \cos(\chi - \Phi), \quad (4.13)$$

$$\begin{aligned} \cos \phi = & \left[\sin^2 \gamma \cos \theta_D \cos \Theta + \sin \theta_D \sin \Theta \cos \Phi \right. \\ & - \sin \gamma \cos \gamma (\sin \Theta \cos \theta_D \cos(\Phi - \chi) + \sin \theta_D \cos \Theta \cos \chi) \\ & \left. - \sin^2 \gamma \sin \theta_D \sin \Theta \cos(\Phi - \chi) \cos \chi \right] / (\sin \theta_\epsilon \sin \theta). \end{aligned} \quad (4.14)$$

Substitution of equations (4.12–4.14) into equation (4.7) yields an expression for the full 3D laboratory frame angular distribution of the photofragments. Simulation of the measured TOF profiles requires integration of this expression over all photofragments with the same velocity projection along the TOF axis. The azimuthal angle χ describes all photofragments with the same TOF shift whilst $\cos \gamma$ is proportional to the TOF shift⁴⁰ and therefore, integration over all values of χ from 0 to 2π yields an expression for the measured profile in terms of the TOF shift, $x = \cos \gamma$, of the

form,

$$I = g_0 + g_2 P_0^2(x) + g_4 P_0^4(x), \quad (4.15)$$

where $P_0^k(x)$ are Legendre polynomials in terms of the TOF shift and g_k are coefficients which will depend on the probe transition sensitivity factors, s_k , the translational anisotropy parameter, β , and alignment parameters, $a_q^{(k)}(p)$.

4.2.2 Experimental geometries

As discussed in chapter 3, the polarisation parameters were determined from fitting simulations to the sum and difference of TOF profiles taken in multiple experimental geometries. The data analysis was exactly the same as described in chapter 3 except that the expressions for the simulated TOF profiles were determined in terms of the molecular-frame polarisation parameters. All experimental geometries used were as described in chapter 3 and illustrated in figure 3.1, with the direction of ϵ_{phot} defined by its angle from the TOF axis, θ_D , before and the direction of ϵ_{probe} is now defined by its angle from the TOF axis, Θ , instead of χ_P .

4.2.2.1 The (Cl + Cl*) dissociation channel

For the electronically excited Cl* photofragment, $J = 1/2$ and all the polarisation parameters with $k > 1$ appearing in equation (4.7) are zero and consequently the molecular-frame detection probability is simply given by,

$$I_{\text{det}} = 1 + \beta P_2(\cos \theta_\epsilon) + 2s_1 \sin \theta_\epsilon \cos \theta_\epsilon \text{Im}[a_1^{(1)}(\parallel, \perp)] C_1^1(\theta) \sin \phi. \quad (4.16)$$

The parameters describing the core extraction and temporal width of the probe laser were once again determined from fitting to experimental profiles taken in geometry G_1 ($\theta_D = 54.7^\circ$, $\Theta = 54.7^\circ$, $\Phi = 0$). In this geometry the laboratory frame detection probability for Cl* is constant and the only deviations from a theoretical “top-hat” profile are due to core extraction and the probe laser temporal width as illustrated in figure 2.4.

The translational anisotropy was determined by fitting simulations to the line-shape of the sum and difference of TOF profiles taken in geometry pair G_3 ($\theta_D = 0^\circ/90^\circ, \Theta = 54.7^\circ, \Phi = 0$). The laboratory-frame detection probabilities for these geometries are calculated to be,

$$I_{Hma} = 1 + \beta P_0^2(x), \quad (4.17)$$

$$I_{Vma} = 1 - \frac{1}{2}\beta P_0^2(x). \quad (4.18)$$

The coherent orientation parameter, $\text{Im}[a_1^{(1)}(\parallel, \perp)]$, is proportional to the $\beta_0^2(2, 1)$ bipolar moment described in chapter 3 in the high- J limit. Whilst these two parameters have very different mechanistic origins, they will transform in the same way under rotation and, as with the $\beta_0^2(2, 1)$ parameter, the sensitivity to the $\text{Im}[a_1^{(1)}(\parallel, \perp)]$ parameter is maximised when $\theta_D = 45^\circ$. This parameter was therefore determined by fitting to the difference between profiles taken with left and right circular polarised probe light in geometry pair G_5 ,

$$I_{45\text{circ}} = 1 + \frac{1}{4}\beta + s_1 \frac{1}{\sqrt{2}} \text{Im}[a_1^{(1)}(\parallel, \perp)]. \quad (4.19)$$

4.2.2.2 The (Cl + Cl) dissociation channel

For the (Cl + Cl) dissociation channel, the initial photon absorption is well-known to be to the C $^1\Pi_{1u}$ state so that only incoherent perpendicular polarisation parameters are non-zero and therefore, by setting the weighting factors appearing in equation (4.7) to be for a pure perpendicular transition ($\beta = -1$), the molecular-frame detection probability is simplified to be,

$$I_{\text{det}} = 1 + \beta P_2(\cos \theta_\epsilon) + \frac{3}{2}s_2 \sin^2 \theta_\epsilon \left(a_0^{(2)}(\perp) C_0^2(\theta) + 2a_2^{(2)}(\perp) C_2^2(\theta) \cos 2\phi \right). \quad (4.20)$$

This expression is subsequently transformed into the laboratory frame for each experimental geometry using equations (4.12 – 4.14). The parameters describing the

core extraction and temporal width of the probe laser were assumed to be the same as for the (Cl + Cl*) channel since these were found to be insensitive to the photolysis wavelength used and β parameters were determined from the sum and difference of profiles taken in geometry pair G_3 using equations (4.17) and (4.18). The laboratory-frame detection probability obtained from the transformation of equation (4.20) shows that there is, in fact, a small contribution from the angular momentum alignment parameters when detecting Cl atoms in geometry pair G_3 . It was found that inclusion of alignment parameters in the fitting routine had a negligible effect on the returned β parameters and therefore the neglect of alignment effects in this case is justified.

The alignment parameters, $a_0^{(2)}(\perp)$ and $a_2^{(2)}(\perp)$, were determined from TOF profiles taken geometry pair G_4 for which the laboratory frame detection probability is calculated to be,

$$I_{maH} = 1 + s_2 a_0^{(2)}(\perp) P_0^2(x), \quad (4.21)$$

$$\begin{aligned} I_{maV} = 1 - \frac{1}{10} s_2 \left(a_0^{(2)}(\perp) - 2\sqrt{6} a_2^{(2)}(\perp) \right) + \frac{1}{14} s_2 \left(-5a_0^{(2)}(\perp) + 4\sqrt{6} a_2^{(2)}(\perp) \right) P_0^2(x) \\ + \frac{1}{70} s_2 \left(-3a_0^{(2)}(\perp) + \sqrt{6} a_2^{(2)}(\perp) \right) P_0^4(x). \end{aligned} \quad (4.22)$$

As can be seen from these equations, the TOF profiles taken in these geometries are sensitive to both $a_0^{(2)}(\perp)$ and $a_2^{(2)}(\perp)$ parameters and therefore, in order to ensure that the true values of these parameters were returned by the fitting routine, TOF profiles were also recorded in geometry pair G_2 . The ratio of intensities of profiles taken in this geometry pair were used to calculate the $\beta_0^2(0, 2)$ parameter using equation (3.11) which, in the high- J limit for a pure perpendicular transition, is related to the molecular-frame polarisation parameters by the equation,⁴⁰

$$\beta_0^2(0, 2) = -\frac{1}{4} a_0^{(2)}(\perp) + \frac{\sqrt{6}}{2} a_2^{(2)}(\perp). \quad (4.23)$$

In the fitting routine for the data taken in geometry pair G_3 , only $a_0^{(2)}(\perp)$ was varied and $a_2^{(2)}(\perp)$ was determined from the experimentally measured $\beta_0^2(0, 2)$ parameter using the relationship given in equation (4.23).

4.3 Results

4.3.1 The (Cl + Cl*) dissociation channel

TOF profiles of the Cl* photofragments produced *via* the (Cl + Cl*) dissociation channel were taken at three specific wavelengths; 320, 325 and 330 nm. The atomic fragments detected in this work have much higher velocities than the NO molecular fragments probed in the previous chapter with, for example, ³⁵Cl* atoms produced in conjunction with ³⁵Cl following dissociation at 320 nm having velocities of 1900 ms⁻¹ and as a consequence, both Doppler selection and core extraction will affect the observed profiles more significantly. The high velocity of the photofragments will mean that the probe transition will have a relatively large Doppler width. This has been measured to be approximately 0.8 cm⁻¹ which is close to the bandwidth of the probe laser (~ 1 cm⁻¹) and therefore the shape of the measured TOF profiles changes as the probe laser is scanned over the probe transition as different photofragment velocities are detected.⁵⁰ This Doppler selection was accounted for by stepping the probe laser over the full Doppler width of the probe transition with regular steps of 0.0005 nm symmetrically distributed about the centre of the probe transition. Higher photofragment velocities will also mean that more ions will miss the detector, resulting in core extraction becoming more significant. For all experiments described in this chapter, both isotopes of the probed photofragment were detected simultaneously with the expected difference in the ion TOF for each photofragment meaning that the measured profiles for each isotope were sufficiently separated in time so that they did not overlap. A sample raw TOF profile of the electronically excited Cl* photofragments taken in geometry G_1 following dissociation at 325 nm

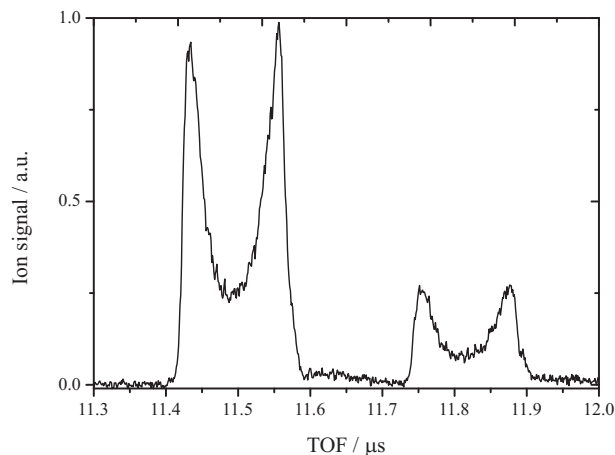


Figure 4.3: Sample raw TOF profiles showing both $^{35}\text{Cl}^*$ (left) and $^{37}\text{Cl}^*$ (right) photofragments produced following dissociation at 325 nm taken in geometry G_1 .

is shown in figure 4.3 where both $^{35}\text{Cl}^*$ and $^{37}\text{Cl}^*$ photofragments are clearly seen.

Both profiles have a significant dip in the centre, which is much more pronounced than for the NO photofragments probed in figure 3.10, reflecting the more significant contribution from core extraction and Doppler selection. This effect was modelled using the parameters described in chapter 2 and figure 4.4 shows sample area normalised and symmetrised TOF profiles for both $^{35}\text{Cl}^*$ and $^{37}\text{Cl}^*$ photofragments produced following dissociation at 325 nm taken in geometry G_1 together with fitted simulations. As mentioned in the previous chapter, the only deviations from an ideal, “top-hat” profile in this geometry will be due to these effects as well as the temporal width of the probe laser and the good agreement between the experimental and theoretical profiles demonstrates that these experimental effects are well accounted for.

The translational anisotropy of the Cl^* fragments was subsequently determined by fitting simulations to the sum and difference of experimental TOF profiles taken in geometry pair G_3 . Sample sum and difference profiles for both the $^{35}\text{Cl}^*$ and $^{37}\text{Cl}^*$ photofragments produced following dissociation at 330 nm taken in this geometry pair are shown in figure 4.5 together with fitted simulations. The measured β parameters are shown in table 4.1, with the measured β parameters for the two

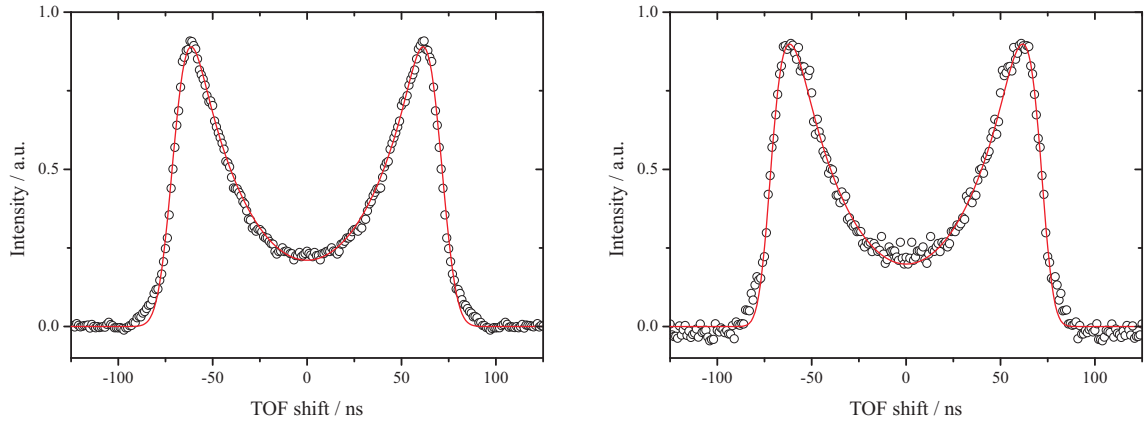


Figure 4.4: Sample TOF profiles (open circles) and fitted simulations (solid line) for both $^{35}\text{Cl}^*$ (left) and $^{37}\text{Cl}^*$ (right) photofragments produced following dissociation at 325 nm taken in geometry G_1 .

isotopes in good agreement with each other. The translational anisotropy clearly has a strong dependence on the dissociation wavelength, with the transition being predominantly perpendicular at 320 nm and predominantly parallel at 330 nm.

Table 4.1: The measured β parameters for the Cl^* photofragments produced *via* the $(\text{Cl} + \text{Cl}^*)$ channel.

Fragment	Wavelength / nm		
	320	325	330
$^{35}\text{Cl}^*$	-0.30 ± 0.07	-0.06 ± 0.04	0.32 ± 0.07
$^{37}\text{Cl}^*$	-0.28 ± 0.08	-0.07 ± 0.05	0.40 ± 0.09

Finally, the electronic angular momentum orientation of the Cl^* photofragments is determined by fitting simulations to the difference between experimental profiles taken in geometry pair G_5 . Sample difference profiles and simulated fits for the $^{35}\text{Cl}^*$ and $^{37}\text{Cl}^*$ fragments produced following dissociation at 320 nm are shown in figure 4.6 and a significant difference in the measured difference profiles for the two isotopes is now seen. The measured $\text{Im}[a_1^{(1)}(\parallel, \perp)]$ parameters are shown in table 4.2 and it is clear that for all dissociation wavelengths, unlike the translational

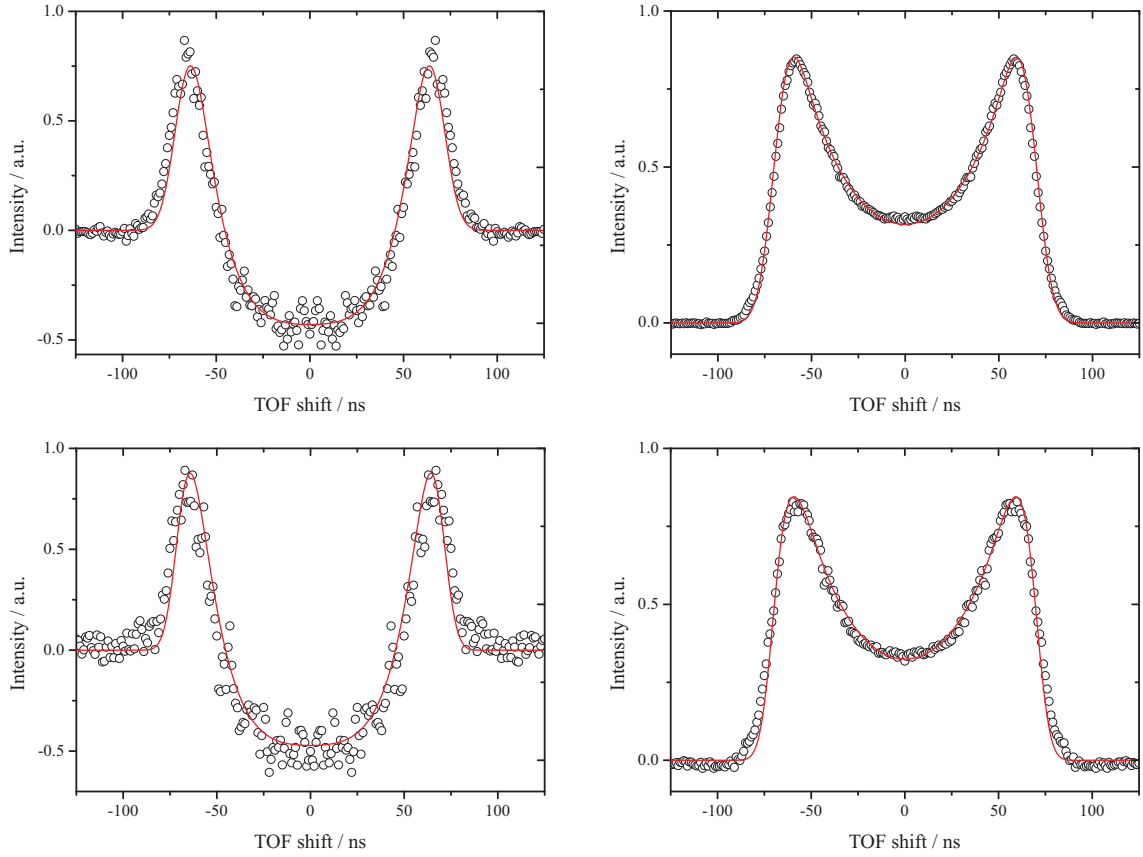


Figure 4.5: Sum (right) and difference (left) of experimental TOF profiles (open circles) taken in geometry pair G_3 together with fitted simulations (solid line) for both $^{35}\text{Cl}^*$ (top) and $^{37}\text{Cl}^*$ (bottom) photofragments produced following dissociation at 330 nm.

anisotropy, the measured orientation depends on the isotope probed.

Table 4.2: The measured $\text{Im}[a_1^{(1)}(\parallel, \perp)]$ parameters for the Cl^* photofragments produced *via* the $(\text{Cl} + \text{Cl}^*)$ channel.

Fragment	Wavelength / nm		
	320	325	330
$^{35}\text{Cl}^*$	0.18 ± 0.06	0.13 ± 0.04	0.06 ± 0.03
$^{37}\text{Cl}^*$	0.07 ± 0.06	0.01 ± 0.08	-0.07 ± 0.06

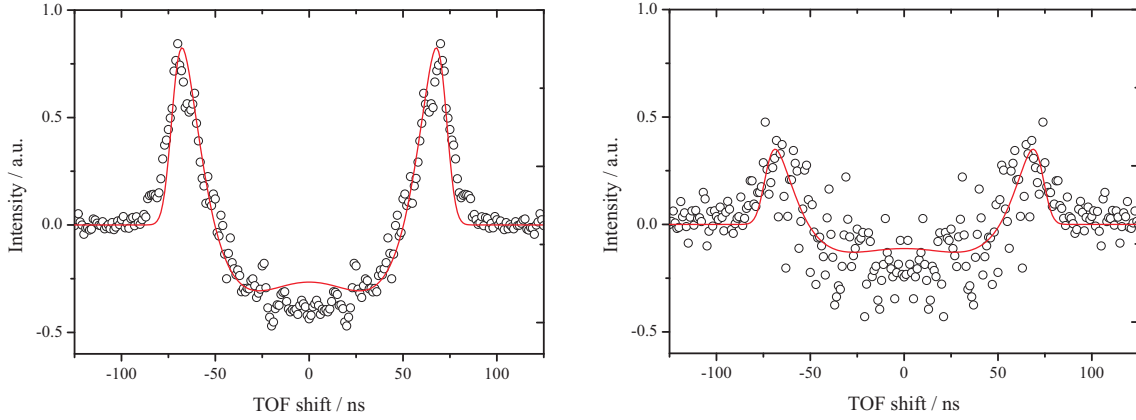


Figure 4.6: Experimental difference TOF profiles (open circles) taken in geometry pair G_5 together with fitted simulations (solid line) for both $^{35}\text{Cl}^*$ (left) and $^{37}\text{Cl}^*$ (right) photofragments produced following dissociation at 320 nm.

4.3.2 The (Cl + Cl) dissociation channel

TOF profiles were also taken of the ground state Cl photofragments produced *via* the (Cl + Cl) channel for four dissociation wavelengths; 320, 330, 340 and 350 nm. Firstly, the translational anisotropy was determined from fitting simulations to the sum and difference of profiles taken geometry pair G_3 . Sample sum and difference experimental profiles for both the ^{35}Cl and ^{37}Cl photofragments produced following dissociation at 340 nm taken in this geometry pair are shown in figure 4.7 together with best-fit simulations. The measured β parameters are shown in figure 4.3 and for all dissociation wavelengths and isotopes probed are close to the limiting value of -1 , as expected for a pure perpendicular excitation to the $\text{C } ^1\Pi_{1u}$ state.

Table 4.3: The measured β parameters for the Cl photofragments produced *via* the (Cl + Cl) channel.

Fragment	Wavelength / nm			
	320	330	340	350
^{35}Cl	-0.92 ± 0.05	-0.95 ± 0.05	-0.98 ± 0.05	-0.95 ± 0.06
^{37}Cl	-0.96 ± 0.08	-0.99 ± 0.08	-0.96 ± 0.07	-0.97 ± 0.07

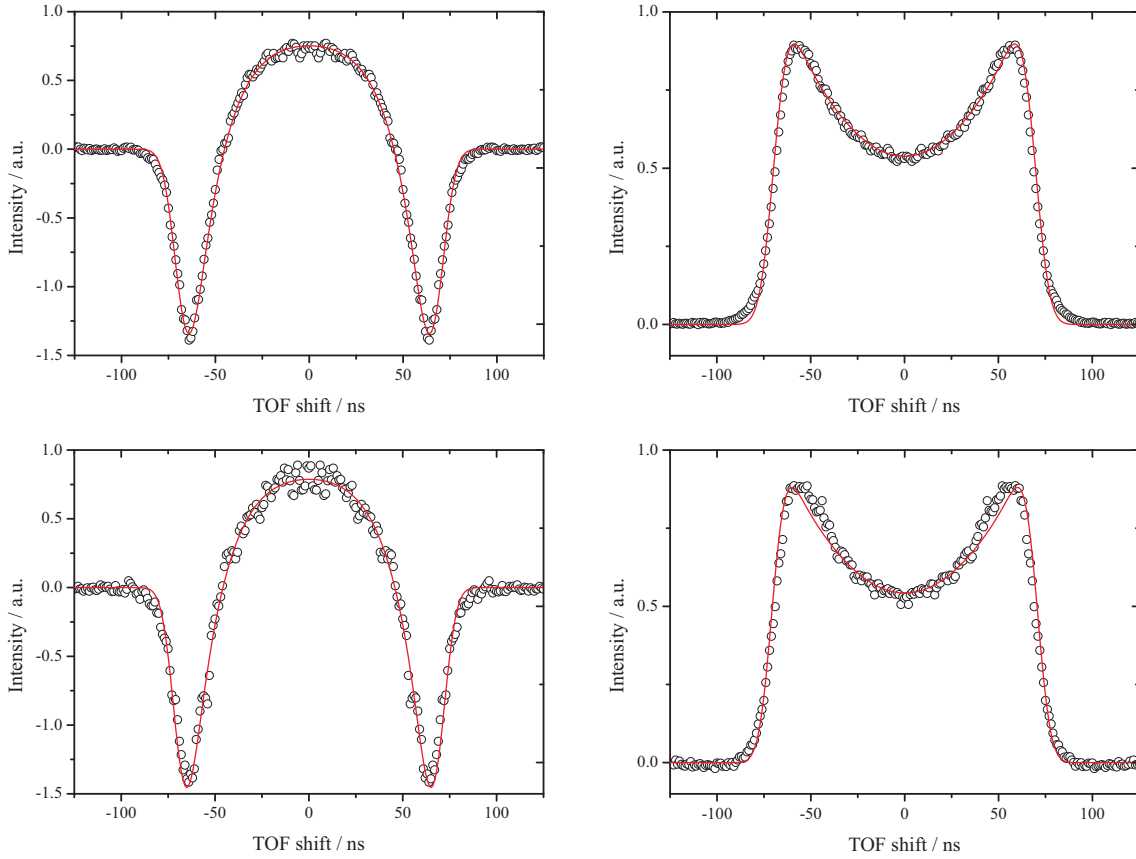


Figure 4.7: Sum (right) and difference (left) experimental TOF profiles (open circles) taken in geometry pair G_3 together with fitted simulations (solid line) for both ^{35}Cl (top) and ^{37}Cl (bottom) photofragments produced following dissociation at 340 nm.

In order to determine the alignment of the Cl photofragments, the $\beta_0^2(0,2)$ parameter was determined from the ratio of areas of TOF profiles taken in geometry pair G_2 using equation (3.11). Sample raw experimental TOF profiles for Cl fragments following dissociation at 320 nm taken in this geometry pair are shown in figure 4.8 and it was found that $\beta_0^2(0,2) = 0.24 \pm 0.05$ for all dissociation wavelengths and all subsequent fits were determined by constraining the two alignment parameters, $a_0^{(2)}(\perp)$ and $a_2^{(2)}(\perp)$, so that equation (4.23) equals this value. The two alignment parameters were subsequently determined by fitting simulations to experimental sum and difference profiles taken in geometry pair G_4 . Sample sum and difference profiles for both the ^{35}Cl and ^{37}Cl photofragments produced following

dissociation at 350 nm taken in this geometry pair are shown in figure 4.9 together with fitted simulations. The measured values of $a_0^{(2)}(\perp)$ and $a_2^{(2)}(\perp)$ are shown in table 4.4 and it is clear that both alignment parameters are (relatively) insensitive to both the photolysis wavelength and the isotope probed.

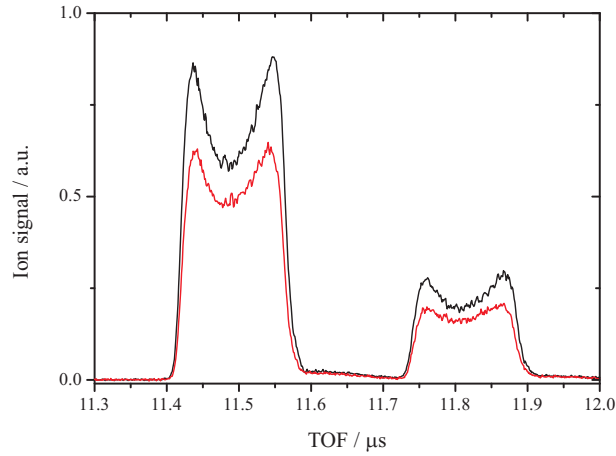


Figure 4.8: Raw experimental TOF profiles taken in geometry pair G_2 , with the photolysis laser horizontally polarised and the probe laser horizontally (black) and vertically (red) polarised for both ^{35}Cl (left) and ^{37}Cl (right) photofragments produced following dissociation at 320 nm.

Table 4.4: The measured $a_0^{(2)}(\perp)$ and $a_2^{(2)}(\perp)$ parameters for the Cl photofragments produced *via* the (Cl + Cl) channel.

Parameter	Fragment	Wavelength / nm			
		320	330	340	350
$a_0^{(2)}(\perp)$	^{35}Cl	-0.66 ± 0.1	-0.58 ± 0.11	-0.59 ± 0.09	-0.56 ± 0.1
	^{37}Cl	-0.68 ± 0.13	-0.58 ± 0.11	-0.61 ± 0.13	-0.62 ± 0.12
$a_2^{(2)}(\perp)$	^{35}Cl	-0.30 ± 0.09	-0.32 ± 0.08	-0.32 ± 0.06	-0.31 ± 0.09
	^{37}Cl	-0.34 ± 0.1	-0.31 ± 0.09	-0.32 ± 0.1	-0.32 ± 0.1

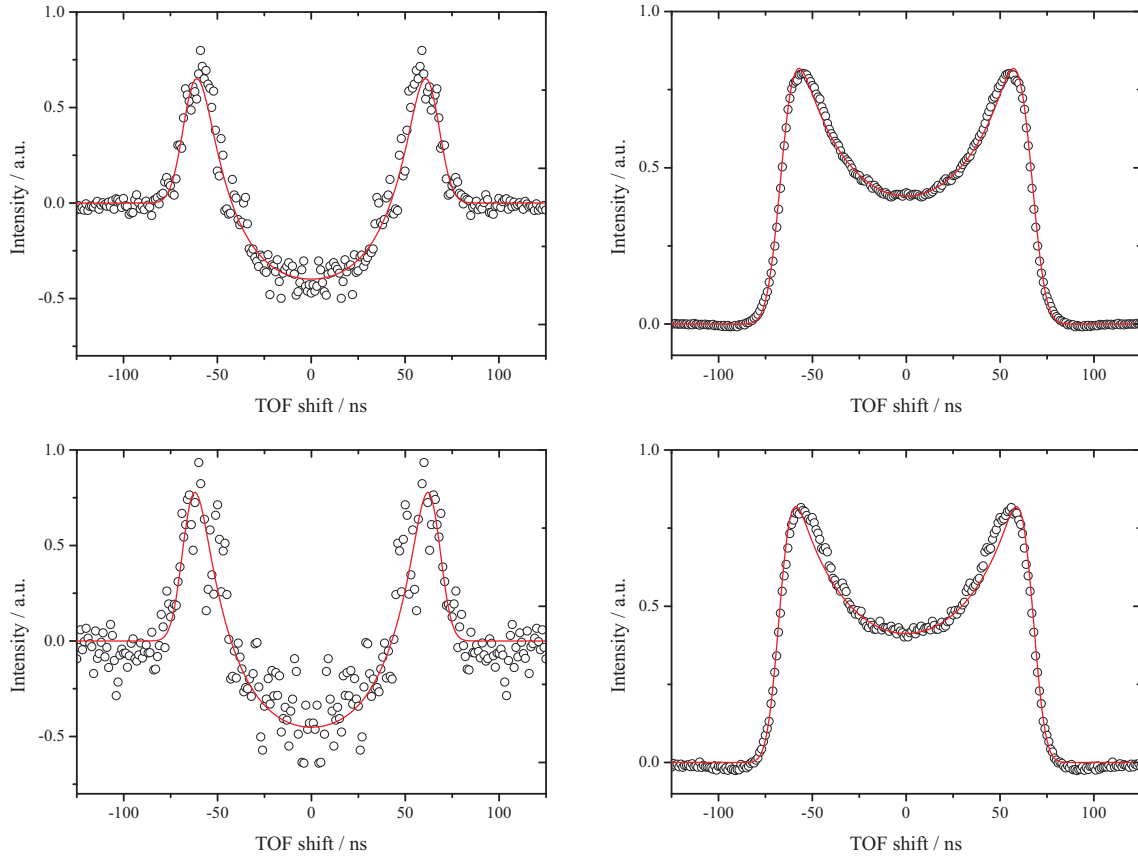


Figure 4.9: Sum (right) and difference (left) experimental TOF profiles (open circles) taken in geometry pair G_4 together with fitted simulations (solid line) for both ^{35}Cl (top) and ^{37}Cl (bottom) photofragments produced following dissociation at 350 nm.

4.4 Discussion

4.4.1 Translational anisotropy

For the (Cl + Cl) dissociation channel, the measured β parameters are all close to their limiting value of -1 as expected for a pure perpendicular transition to the C $^1\Pi_{1u}$ state. The Cl^{*}/Cl branching ratio over the wavelength range studied here has been measured by Samartzis *et al.*⁸ and is found to be less than 1% for wavelengths in the range (320 – 350) nm, therefore indicating that contributions from Cl fragments produced *via* the electronically excited (Cl + Cl^{*}) channel are negligible. This near-limiting translational anisotropy is consistent with previous experimen-

tal measurements for the same dissociation channel at longer wavelengths²⁵ and over the same wavelength range^{8,19,21} with, for example, Rakitzis *et al.*²¹ measuring $\beta = -1 \pm 0.03$ for dissociation at 355 nm. Bass *et al.*²² have measured a slightly reduced translational anisotropy of $\beta = -0.88 \pm 0.03$ for dissociation at 308 nm which they attributed to parent molecular rotations. The reduction in the measured translational anisotropy for a one-photon dissociation of a diatomic molecule due to parent molecular rotations was discussed in chapter 1 and this will affect the measured β parameters shown in table 4.3, which are all slightly reduced from the expected limiting value of -1 . This reduction in the measured translational anisotropy due to parent molecular rotations is quantified by calculating the depolarisation factor, β_{depol} , using equation (1.3). The rotational angular frequency, ω , of the parent Cl₂ molecule is estimated classically using the expression,

$$E_{\text{rot}} = \frac{1}{2}I\omega^2, \quad (4.24)$$

where the rotational energy, E_{rot} , is determined from the molecular beam rotational temperature of 140 K and I is calculated from the Cl₂ rotational constant of $B = 0.243 \text{ cm}^{-1}$.¹⁰ It is therefore found that $\omega = 1.83 \times 10^{12} \text{ s}^{-1}$ which, together with a reasonable estimate of the excited state lifetime of 70 fs,²⁶ gives a value of β_{depol} of 0.95. After correcting the measured β parameters by this factor, all measured values are now within error of -1 and in agreement with previous experimental measurements which used rotationally colder, skimmed molecular beam sources.

The measured alignment and orientation parameters will also be affected by parent molecular rotations, since the renormalisation in equation (4.7) to express the photofragment alignment relative to unpolarised photofragments with an isotropic scattering distribution assumed that the scattering angular distribution, $I(\theta_c)$, was in the fast-recoil limit and therefore any process which reduces the measured value of β may also affect the measured alignment. The reduction in the measured alignment due to parent molecular rotations has been described by both Kuznetsov *et al.*⁵¹ and Bougas *et al.*⁵² and will be discussed in more detail in the next chapter, where

lifetime depolarisation effects are found to be more significant. For the dissociation of Cl₂ discussed in this chapter, however, the reduction in measured alignment parameters due to these effects is expected to be less than 2% and may therefore be neglected. For example, Bougas *et al.*⁵² have shown that the $\text{Re}[A_2^2]$ parameter, which is proportional to the $a_2^{(2)}(\perp)$ parameter measured in this work,⁴⁹ will be reduced, for a one-photon dissociation, by the factor,

$$\frac{(1 + \cos \gamma)^2}{4}, \quad (4.25)$$

where γ is the classical angle through which the parent molecule has rotated in the time between initial photon absorption and dissociation. A semi-classical interpretation of this depolarisation factor may be determined, using the same method as Jonah⁵³ to determine equation (1.3), by defining this angle, γ , as (ωt) with the probability that a molecule will dissociate in a time period t is given by $(1/\tau)e^{-t/\tau}$. The factor, $a_{2,\text{depol}}^{(2)}$, by which $a_2^{(2)}(\perp)$ will be reduced is therefore calculated to be,

$$\begin{aligned} a_{2,\text{depol}}^{(2)} &= \frac{1}{\tau} \int_0^\infty \frac{(1 + \cos(\omega t))^2}{4} e^{-t/\tau} dt \\ &= \frac{1}{8} \left(3 + \frac{4}{1 + (\omega\tau)^2} + \frac{1}{1 + 4(\omega\tau)^2} \right). \end{aligned} \quad (4.26)$$

Using the values of ω and τ used previously to determine β_{depol} , $a_{2,\text{depol}}^{(2)}$ is calculated to be 0.984.

For the (Cl + Cl*) dissociation channel, the measured translational anisotropy now has a clear dependence on the dissociation wavelength used. This wavelength dependence results from the competition between two transitions of different symmetry whose excited states decay into the (Cl + Cl*) dissociation channel. At short wavelengths, a perpendicular transition dominates which, as mentioned previously, is thought to be excitation to the C ¹Π_{1u} state followed by non-adiabatic coupling with the excited (1) ³Σ_{1u}⁺ state which correlates adiabatically with the (Cl + Cl*) limit.^{11,14} At longer wavelengths, a parallel transition dominates which itself is a

spin-forbidden transition to the B $^3\Pi_{0+u}$ state⁶⁻⁸ partially allowed due to spin-orbit mixing between the ground X $^1\Sigma_{0g}^+$ state and excited $^3\Sigma_g^-$ states.¹¹ An equal contribution from both parallel and perpendicular transitions will result in a β parameter of +0.5 and therefore the measured translational anisotropy indicates that at 330 nm there is a near equal contribution from parallel and perpendicular transitions, with the perpendicular transition becoming increasingly dominant as the wavelength is reduced to 320 nm. Clearly the measured translational anisotropy for the Cl* photofragments measured here will be subject to the same depolarisation factor, $\beta_{\text{depol}} = 0.95$, as the ground state fragments. However, in this case the small correction to the measured values due to this factor is insignificant compared to the quoted errors.

Samartzis *et al.*⁸ have also measured the translational anisotropy of the $^{35}\text{Cl}^*$ fragments using ion imaging and found that $\beta = -0.33 \pm 0.05$, -0.06 ± 0.05 and 0.24 ± 0.05 at 320, 325 and 330 nm respectively, in good agreement with the results observed in this work. The observed results are, however, in disagreement with the β parameters calculated using the quantum mechanical calculations of Johnsen *et al.*²⁶ which reproduces the measured Cl*/Cl branching ratio and the general trend in β , changing from +2 at high wavelengths to -1 at shorter wavelengths, but predicts this change to occur at slightly longer wavelengths than observed experimentally. The calculated wavelength dependence of the β parameter will be sensitive to the relative shapes of the B $^3\Pi_{0+u}$ and C $^1\Pi_{1u}$ potential energy surfaces as well as the exact crossing point of the C $^1\Pi_{1u}$ and (1) $^3\Sigma_{1u}^+$ surfaces. Very small changes to the *ab initio* potential energy curves would cause these discrepancies between experiment and theory and are likely to be the cause of this wavelength shift.^{25,26}

4.4.2 Ground state photofragment alignment

Previous measurements of the $a_0^{(2)}(\perp)$ and $a_2^{(2)}(\perp)$ parameters for the Cl photofragments produced *via* the (Cl + Cl) channel are shown in table 4.5 and are generally in good agreement with the values measured in this work. It appears that the

discrepancy in the measured values at 355 nm^{19,21} is simply a problem of comparing results taken in different laboratories and this work has confirmed that both the $a_0^{(2)}(\perp)$ and $a_2^{(2)}(\perp)$ parameters remain relatively constant over the wavelength range (320–350) nm. The measured values are generally in good agreement with the quantum mechanical calculations of Johnsen *et al.*,²⁶ who calculated that $a_0^{(2)}(\perp) = -0.7$ and $a_2^{(2)}(\perp) = -0.26$ over this wavelength range. The measured $a_0^{(2)}(\perp)$ parameters are slightly less negative than calculated, whilst the measured $a_2^{(2)}(\perp)$ parameters are slightly more negative. As will be discussed in more detail later, the magnitudes of these parameters may be related to the non-adiabatic transition probability from the C ¹Π_{1u} state to the A ³Π_{1u} state and it therefore seems that the quantum mechanical calculations may slightly underestimate the extent of these non-adiabatic transitions in the dissociation process.

Table 4.5: Previous measurements of the $a_0^{(2)}(\perp)$ and $a_2^{(2)}(\perp)$ parameters for the Cl photofragments produced *via* the (Cl + Cl) channel.

Photolysis wavelength / nm	$a_0^{(2)}(\perp)$	$a_2^{(2)}(\perp)$
308 ²²	-0.62 ± 0.09	-0.26 ± 0.07
320 ²⁰	-0.50 ± 0.10	-0.32 ± 0.06
355 ²¹	-0.50 ± 0.10	-0.30 ± 0.10
355 ¹⁹	-0.35 ± 0.04	-0.15 ± 0.04

The magnitude of the incoherent, $a_0^{(2)}(\perp)$, polarisation parameter may be predicted by expanding the molecular electronic wavefunction, Ψ_{elec} , for short internuclear distances, R , adiabatically in terms of the atomic basis at large R ,^{33,54,55}

$$\Psi_{\text{elec}}^{n\Omega} \xrightarrow{R \rightarrow \infty} \sum_{M_a M_b} T_{J_a, M_a, J_b, M_b}^{n\Omega} \hat{A} |J_a, M_a\rangle |J_b, M_b\rangle, \quad (4.27)$$

where the subscripts, a or b , denote the specific atomic fragment and M_a and M_b are the projections of the total angular momenta J_a and J_b respectively along the internuclear axis. Ω is the projection of the total molecular angular momentum along

the internuclear axis and is equal to $M_a + M_b$ and different Hund's case (c) states with the same Ω are distinguished by the index n . The operator $\hat{A}$ ensures that the wavefunction is antisymmetric with respect to electron exchange.⁵⁵ The long range expansion coefficients, $T_{J_a, M_a, J_b, M_b}^{n\Omega}$, are determined by considering long range terms of the interatomic part of the Coulomb interaction potential, $V(R)$. At large R , this potential may be expanded as a power series in terms of R^{-1} .⁵⁶ Cl₂ will not have a non-vanishing dipole-dipole interaction ($V \sim R^{-3}$), since this only occurs for like atoms with different parity,⁵⁵ and therefore the leading first-order interaction term in the expansion is the quadrupolar-quadrupolar interaction ($V \sim R^{-5}$). The expansion coefficients, $T_{J_a, M_a, J_b, M_b}^{n\Omega}$, and interaction energies of the adiabatic states have been tabulated by Alexander⁵⁵ by diagonalising the quadrupolar-quadrupolar interaction matrix at large R .

In the adiabatic limit, the non-crossing rule applies to wavefunctions with the same value of Ω and therefore the energy ordering of Hund's case (c) molecular states at short range will be maintained until dissociation so that molecular case (c) states can be matched directly to product atomic states.¹³ It can therefore be shown that for the C ¹Π_{1u} state, the molecular wavefunction can be written as,

$$\Psi_{\text{elec}}^{\text{C } ^1\Pi_{1u}} \xrightarrow{R \rightarrow \infty} |3/2, 1/2\rangle |3/2, 1/2\rangle, \quad (4.28)$$

where the expansion coefficient, $T_{3/2, 1/2, 3/2, 1/2}^{\text{C } ^1\Pi_{1u}}$, is equal to 1. This wavefunction is for the $\Omega = +1$ component of the C state and the $\Omega = -1$ component is simply given by reversing the sign of the M_J values. The square of the expansion coefficients give the probability that a Cl photofragment will be produced in a particular M_J state and it is therefore clear that for adiabatic dissociation along the C ¹Π_{1u} state, Cl atoms are produced maximally aligned with all their population in $|M_J| = 1/2$. The M_J populations are given by the diagonal elements of the angular momentum density matrix, $\rho_{M_J M_J}$, which, using the properties of the Wigner-3j coefficient appearing

in equation (1.8), are given by the incoherent polarisation parameters with $q = 0$,

$$\rho_{M_J M_J} = \sum_k (-1)^{J-M_J} \frac{(2k+1)[J(J+1)]^{k/2}}{c(k) \langle J || J^{(k)} || J \rangle} \begin{pmatrix} J & k & J \\ -M_J & 0 & M_J \end{pmatrix} A_0^{(k)}. \quad (4.29)$$

For a pure parallel or perpendicular transition, the $A_0^{(k)}$ polarisation parameters are equivalent to the molecular-frame $a_0^{(k)}(p)$ parameters and therefore this equation may be used to relate the measured incoherent polarisation parameters to the photofragment M_J populations. Using this equation, the value of $a_0^{(2)}(\perp)$ corresponding to maximally aligned Cl atoms, with all their population in $|M_J| = 1/2$, which will result from a pure adiabatic dissociation along the C state is found to be -0.8 .

The measured $a_0^{(2)}(\perp)$ parameters shown in table 4.4 are all clearly significantly reduced from this limiting value and therefore the dissociation mechanism must not be purely adiabatic along the C state. Like the C state, the A $^3\Pi_{1u}$ state may be shown to correlate adiabatically at long R to an expansion over the atomic basis,^{19,21}

$$\Psi_{\text{elec}}^{\text{A } ^3\Pi_{1u}} \xrightarrow{R \rightarrow \infty} \frac{1}{\sqrt{2}} (|3/2, 3/2\rangle |3/2, -1/2\rangle + |3/2, -1/2\rangle |3/2, 3/2\rangle), \quad (4.30)$$

where, as before, the $\Omega = -1$ component is given by reversing the sign of the M_J values. Adiabatic dissociation along this state will therefore produce photofragments where all possible M_J states, $|M_J| = 1/2$ and $3/2$, are equally populated and consequently the incoherent alignment parameter, $a_0^{(2)}(\perp)$, resulting from adiabatic dissociation along this state will be equal to zero. Clearly, therefore, non-adiabatic homogeneous transitions from the initially excited C state to the A state will result in a reduction in the observed $a_0^{(2)}(\perp)$ from the limiting value of -0.8 . These non-adiabatic transitions will be of the non-crossing type and are a manifestation of the breakdown of the Born-Oppenheimer approximation.²¹ There are no avoided crossings between the C and A states and therefore these transitions must occur at long R where the magnitude of the energy gap between the two states becomes

comparable to the magnitude of the matrix elements describing the non-adiabatic transitions. The non-adiabatic crossing probability, w , from the C to A state may be simply related to the measured incoherent alignment by the relation,¹⁹

$$a_0^{(2)}(\perp) = -\frac{4}{5}(1 - w). \quad (4.31)$$

Using this equation, the non-adiabatic crossing probability is calculated to be 0.18 ± 0.12 , 0.28 ± 0.12 , 0.26 ± 0.11 and 0.3 ± 0.12 for dissociation at 320, 330, 340 and 350 nm respectively for the ³⁵Cl photofragments. As expected, no significant difference is observed for the ³⁷Cl photofragments since the relatively small difference in the reduced masses of ³⁵Cl₂ and ³⁵Cl³⁷Cl will result in very similar partial cross-sections.²⁶ Asano and Yabushita¹² used their *ab initio* calculations of the potential energy surfaces to obtain a semi-classical prediction of this transition probability by assuming that the non-adiabatic transitions were Rosen-Zener-Demkov (RDZ) type transitions. The RDZ model is a typical model for radial derivative coupling non-adiabatic transitions between adiabatic states of the same symmetry. In this model, the diagonal matrix elements in the diabatic representation are assumed to have a constant energy separation and the diabatic coupling element between the different states depends on the internuclear distance, R , as $A\exp(-\alpha R)$, where A and α are constants which are determined by fitting the energy difference predicted by the RDZ model to the *ab initio* adiabatic potential energy curves.¹¹ Using this model, an approximately constant transition probability is calculated which decreases slightly from 0.257 at 308 nm to 0.251 at 355 nm which is in excellent agreement with the experimentally observed transition probabilities. The slight increase in transition probability as the photolysis wavelength is reduced, predicted by the RDZ model, is consistent with a simple interpretation of the dissociation dynamics based on the Massey parameter.⁵⁷ The Massey criterion, which will be discussed in more detail in the next chapter, states that the probability of a non-adiabatic transition depends on the timescale upon which the system moves through the region of non-adiabatic coupling, t_{system} , relative to the timescale associated with the non-adiabatic transition,

$t_{\text{transition}}$; the diabatic limit will be approached when the ratio of these timescales, $t_{\text{system}}/t_{\text{transition}}$, is much less than one. Therefore, according to the Massey criterion, the non-adiabatic transition probability will increase as t_{system} is reduced which will occur as the wavelength is decreased as more repulsive parts of the potential energy surfaces are accessed. Whilst the measured $a_0^{(2)}(\perp)$ parameters shown in table 4.4 are all relatively constant, there does seem to be a slight increase in $a_0^{(2)}(\perp)$ at longer wavelengths *i.e.* the transition probability is increasing as the wavelength is increased, which is the opposite trend to that predicted by the Massey criterion. This opposite trend has been noted previously by Bass *et al.*²² and it appears that the progressively slower timescales associated with the dissociation in fact facilitate the non-adiabatic transitions. This is confirmed by the quantum mechanical calculations of Johnsen *et al.*²⁶ and is found to have an increasingly significant effect as the wavelength is increased further, with the measured alignment being close to zero as the photolysis wavelength approaches the dissociation limit.²⁵

Further evidence for the existence of non-adiabatic transitions in the dissociation mechanism is given by the measurement of a non-zero $a_2^{(2)}(\perp)$ polarisation parameter, which arises from the coherent excitation of the degenerate $\Omega = \pm 1$ components of the C state which are approximately equally populated by the initial absorption step.²⁶ The coherently excited $\Omega = \pm 1$ components of the C state may dissociate adiabatically along the C state, both undergo a non-adiabatic transition and dissociate along the A state or one component may undergo a non-adiabatic transition and dissociate as a coherent superposition of the C $\Omega = \pm 1$ and A $\Omega = \mp 1$ sub-states. The $a_2^{(2)}(\perp)$ parameter describes the coherence between pairs of atomic photofragment states with M_J and $M_J \pm 2$ ²³ which, according to the adiabatic expansions of the C and A states over the atomic basis, are not present if both $\Omega = \pm 1$ sub-states dissociate along the same potential energy surface A or C. If, however, the dissociation occurs as a coherent superposition of the C $\Omega = \pm 1$ and A $\Omega = \mp 1$ sub-states then atomic photofragment states with M_J and $M_J \pm 2$ will exist and a non-zero $a_2^{(2)}(\perp)$ may be observed. The measured $a_2^{(2)}(\perp)$ may be expressed in terms of the

phase difference, $\cos \Delta\Phi$, between the $\Omega = \pm 1$ sub-states and the non-adiabatic crossing probability, w ,^{19,58}

$$a_2^{(2)}(\perp) = \frac{4}{5} \sqrt{w(1-w)} \cos \Delta\Phi. \quad (4.32)$$

Using this equation to determine $\Delta\Phi$ using the values of w obtained from the $a_0^{(2)}(\perp)$ parameters will clearly have a very large error⁵⁰ so an analysis of the exact calculated values is not possible but it does appear that $\cos \Delta\Phi$ is relatively constant for all dissociation wavelengths and close to its limiting value of -1 . As mentioned previously, the non-adiabatic transition between the C and A states will occur at large R , when the two adiabatic states are close in energy, and therefore adiabatic motion along the different potential energy surfaces after crossing is not expected to contribute to $\Delta\Phi$. The phase difference must therefore result from the “dynamical phase”, the phase difference resulting from non-adiabatic transitions,¹¹ which is independent of dissociation energy and is clearly particularly large for Cl₂ dissociation.⁵⁹

The near-limiting measured β parameters and the excellent agreement between the measured alignment and theoretical predictions indicates that the assumption that $\beta = -1$ in equation (4.20) is valid. If there was a small contribution from a perpendicular transition then additional incoherent $a_0^{(2)}(\parallel)$ as well as coherent $\text{Re}[a_1^{(2)}(\parallel, \perp)]$ parameters would contribute to the observed photofragment alignment. Campbell *et al.*²⁵ have measured non-zero values for the coherent, γ_2 , polarisation parameter, which is directly related to the $\text{Re}[a_1^{(2)}(\parallel, \perp)]$ parameter,¹ therefore indicating a small contribution from a parallel transition. They attributed this contribution to be due to either spin-orbit coupling of the ground state to higher triplet *gerade* states allowing a weak $\Delta\Omega = 0$ to take place to states correlating with the ground state channel or Coriolis coupling between one of the *ungerade* $\Omega = 1$ states with the *ungerade* $\Omega = 0$ state correlating to the ground state channel.²⁵ This parallel contribution does seem to be more important at longer wavelengths, with the value of γ_2 found to be within error of zero at 355 nm, whilst Rakitzis *et al.*²⁰ also found that inclusion of $\text{Re}[a_1^{(2)}(\parallel, \perp)]$ resulted in no appreciable improvement in

the quality of their data fitting. The experimental data were therefore fit including the $\text{Re}[a_1^{(2)}(\parallel, \perp)]$ parameter to see whether this parallel contribution was present in the alignment observed in this work. It was, however, found that the fits were not improved by the inclusion of this parameter and it is therefore concluded to be zero.

4.4.3 Electronically excited photofragment orientation

The measured angular momentum orientation results from the interference between coherently excited dissociating states associated with parallel and perpendicular transitions and may be understood classically by considering the motion of the excited state charge distribution.⁶⁰ In a mixed transition, where states of both parallel and perpendicular symmetry are excited, this charge distribution will oscillate at an intermediate angle between 0 and 90° to the internuclear axis and may therefore be separated into components both parallel and perpendicular to this axis oscillating in phase. As the two components dissociate along two energetically different pathways a phase difference may develop between the parallel and perpendicular components. This phase difference will cause the oscillating charge distribution to have elliptical motion, with pure circular motion occurring when the phase difference is 90°, and the resulting photofragments will consequently also have helicity.²⁰ If only two interfering states are involved in the dissociation, the measured orientation parameter, $\text{Im}[a_1^{(1)}(\parallel, \perp)]$, will depend on the phase difference between the two parallel and perpendicular components, $\Delta\varphi$, as well as the transition amplitude for the parallel and perpendicular transitions, $|A_{\parallel}|$ and $|A_{\perp}|$ respectively,¹¹

$$\text{Im}[a_1^{(1)}(\parallel, \perp)] \propto |A_{\parallel}||A_{\perp}| \sin \Delta\varphi, \quad (4.33)$$

where the product $|A_{\parallel}||A_{\perp}|$ may be determined from the measured translational anisotropy and is proportional to $\sqrt{(1 + \beta)(1 - \beta/2)}$.²⁴

The phase difference for the two dissociating pathways may be understood by considering the de Broglie wavelength, $\lambda(R)$, for the photofragment as a function of

internuclear separation, R , for the two dissociating pathways,⁶⁰

$$\lambda(R) = \frac{h}{\sqrt{2m[E - V(R)]}}, \quad (4.34)$$

where h is Planck's constant, m is the mass of the photofragment, E is the total energy and $V(R)$ is the potential energy as a function of internuclear separation. Therefore, as the molecule dissociates along different potential energy surfaces the wavefunctions associated with each surface will have different de Broglie wavelengths due to the potential energy difference between the two surfaces. At large internuclear separations, if the potential energy surfaces correspond to the same dissociation asymptote this potential energy difference will disappear and their de Broglie wavelengths will become the same again, with a phase difference between the two wavefunctions resulting from the difference in frequencies along the dissociation pathways. This phase difference will depend on the relative shapes of the two potential energy surfaces and therefore measurements of the photofragment orientation provide a sensitive test of the potential energy surfaces involved in the dissociation process. The de Broglie wavelength calculated using equation (4.34) depends on the mass of the dissociating photofragment and therefore an isotopic mass dependence is predicted for the measured orientation.

As discussed previously, the (Cl + Cl*) dissociation channel results from the coherent excitation of both a parallel transition to the B ³Π_{0+u} state and a perpendicular transition to the C ¹Π_{1u} state. Dissociation then proceeds adiabatically along the B state to the (Cl + Cl*) limit, or along the C ¹Π_{1u} state followed by non-adiabatic coupling with the excited (1) ³Σ_{1u}⁺ state, which correlates adiabatically with the (Cl + Cl*) limit^{11,14} and it is interference between these two dissociation channels which results in the measured orientation of the Cl photofragments. Kim *et al.*⁶¹ have measured this coherent orientation of Cl* for multiple wavelengths in the wavelength region (270 – 400) nm and found the measured Im[$a_1^{(1)}(\parallel, \perp)$] to vary sinusoidally with dissociation wavelength for both ³⁵Cl* and ³⁷Cl* photofragments with an envelope to the oscillation determined by $\sqrt{(1 + \beta)(1 - \beta/2)}$.⁶¹ This

sinusoidal variation in the measured orientation is predicted from equations 4.33 and 4.34 since changing the dissociation wavelength will access different parts of the two interfering dissociation pathways resulting in a different phase difference at the dissociation asymptote. Furthermore, a phase shift is seen between the sinusoidally varying orientations of ³⁵Cl* and ³⁷Cl* due to the mass dependence of the de Broglie wavelengths. The values of $\text{Im}[a_1^{(1)}(\parallel, \perp)]$ measured in this work, shown in table 4.2, are all in excellent agreement with these previous experimental measurements with, for example, Kim *et al.*⁶¹ measuring $\text{Im}[a_1^{(1)}(\parallel, \perp)]$ of 0.14 ± 0.1 and 0.07 ± 0.1 for ³⁵Cl* and ³⁷Cl* respectively following dissociation at 320 nm. Campbell *et al.*²⁵ have also measured this orientation at longer wavelengths and the measured orientation is found to be close to zero as would be expected as the β parameter becomes more limiting.

Asano and Yabushita¹¹ have used a Young's double slit model⁶² together with the RDZ approximation for the non-adiabatic transitions to calculate the phase difference resulting from dissociation along the two pathways at different wavelengths using their *ab initio* potential energy surfaces. They then used equation (4.33) to predict the wavelength dependence of $\text{Im}[a_1^{(1)}(\parallel, \perp)]$ and they found that their predictions approximately modeled both the phase and magnitude of the oscillations measured by Kim *et al.*⁶¹ More recently, the quantum mechanical calculations of Johnsen *et al.*²⁶ have evaluated the $\text{Im}[a_1^{(1)}(\parallel, \perp)]$ parameter and approximately predicted the correct frequency of oscillations but disagreed on the magnitude and sign of the measured orientation. The two theoretical calculations for the Cl* photofragments are shown in figure 4.10 together with the experimental results of Kim *et al.*,⁶¹ Campbell *et al.*²⁵ and this work, where the theoretical calculations Johnsen *et al.*²⁶ have had their sign inverted.

Asano and Yabushita¹¹ attributed the differences between their calculations and the experimental measurements to be due to a small fraction of molecules undergoing non-adiabatic transitions from the (1) ³Σ_{1u}⁺ to the (1) ³Δ_{1u} state. Experimental evidence for these non-adiabatic transitions has also been measured by Alexan-

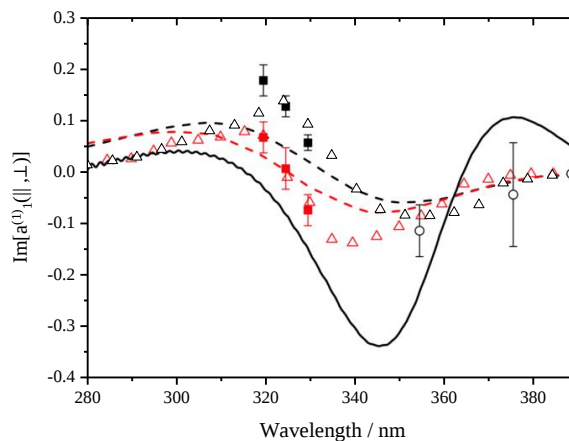


Figure 4.10: The $\text{Im}[a_1^{(1)}(||, \perp)]$ parameters measured in this work (filled squares) for the $^{35}\text{Cl}^*$ (black) and $^{37}\text{Cl}^*$ (red) photofragments. For comparison, the experimental measurements of Kim *et al.*⁶¹ (open triangles) and the theoretical calculations of Asano and Yabushita¹¹ (dashed line) are also shown for both photofragments. The theoretical calculations of Johnsen *et al.*²⁶ (solid line) and ion imaging measurements of Campbell *et al.*²⁵ (open circles) for $^{35}\text{Cl}^*$ photofragments are also shown. The figure is adapted from Ref. 25. Note the sign of the theoretical calculations of Johnsen *et al.*²⁶ has been inverted.

der *et al.*¹⁴ who measured the incoherent orientation parameter, $a_0^{(1)}(\perp)$, which may be observed if circular polarised dissociation light is used. They found that for $^{35}\text{Cl}^*$ atoms produced following dissociation at 310 nm, 88% of the fragments are produced following initial absorption to the $\text{C } ^1\Pi_{1u}$ state, with $67 \pm 16\%$ dissociating along the (1) $^3\Sigma_{1u}^+$ state and $21 \pm 6\%$ dissociating along the (1) $^3\Delta_{1u}$ state. The origin of the sign inconsistency between the measured orientation and theoretical predictions of Johnsen *et al.*²⁶ remains unclear²⁵ and is probably due to some inconsistencies in the conversion between the different polarisation parameter sets.

4.5 Conclusions

This chapter has investigated the UV dissociation of Cl₂ in the wavelength region (320 – 350) nm. Translational anisotropy measurements of the ground state Cl photofragments have shown that dissociation along the ground state (Cl + Cl) pro-

ceeds following a pure perpendicular transition to the C state for wavelengths in the region (320 – 350) nm. However, angular momentum polarisation measurements have shown that dissociation does not occur adiabatically along the C state and that non-adiabatic transitions to the A state at long internuclear distances must occur to explain the observed angular momentum alignment. The extent of these non-adiabatic transitions may be quantified from the polarisation parameters and the measured parameters shown that the variations in the previous measurements over this wavelength range were simply due to the measurements being performed in different laboratories with different techniques and that the extent of non-adiabatic transitions over this range is, in fact, relatively constant and in agreement with the semi-classical predictions of the transition probability calculated by Asano and Yabushita¹² as well as the fully quantum mechanical calculations of Johnsen *et al.*²⁶.

The translational anisotropy of the electronically excited Cl* photofragments has shown that dissociation along the excited state (Cl + Cl*) occurs following a mixed parallel and perpendicular transition to both the B state and the C state. One-photon absorption is found to be predominantly perpendicular, to the C state, at 320 nm and becomes increasingly parallel as the wavelength is increased with parallel absorption to the B state dominating at 330 nm. This mixed parallel and perpendicular is found to result in angular momentum orientation of the Cl* photofragments caused by interference between the two dissociating wavefunctions as they become degenerate at large internuclear distances. This orientation is found to vary sinusoidally with dissociation wavelength as the phase difference between the two wavefunctions depends on the region of the two surfaces initially accessed following one-photon absorption and is found to be consistent with previous experimental and theoretical measurements.^{11,26,61} In addition to being dependent on the dissociation wavelength, the observed orientation is also found to depend on the isotopic mass of the Cl* photofragment probed with the difference between the two observed orientations being found to be consistent with the different de Broglie wavelengths associated with the two isotopic masses probed.

This chapter has shown how the angular momentum polarisation of atomic photofragments may be modelled in terms of a polarisation parameter formalism for the one-photon dissociation of diatomic molecules. In the next chapter it will be shown how this polarisation parameter formalism may be extended to include two-photon dissociations and used to investigate the predissociation of O₂ following two-photon absorption to the C ³Π_g Rydberg state.

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Chapter 5

Predissociation dynamics of the C $^3\Pi_g$ Rydberg state of O₂

In this chapter, O₂ X $^3\Sigma_g^-$ will be excited to the C $^3\Pi_g$ ($v = 0$) and ($v = 1$) Rydberg states *via* two-photon absorption. The O(1D_2) and O(3P_j) photofragments resulting from the predissociation of these states will be detected at various fixed wavelengths within the absorption bands and multiple experimental geometries will be used to determine both the alignment and orientation of the angular momentum of these photofragments. The photofragment alignment is found to be best modelled by a diabatic model, whilst the orientation is attributed to coherent excitation to different spin-orbit components of the C state.

5.1 Introduction

Molecular oxygen plays a major role in atmospheric chemistry and is involved in many important atmospheric processes, including filtering harmful short wavelength UV radiation before it can reach the planetary surface and its photolysis is the first step in the Chapman cycle which leads to formation of the ozone layer.¹ This atmospheric importance has led to numerous experimental and theoretical studies of its UV absorption and photodissociation.^{2,3} The dynamics of one-photon UV dissociation of molecular oxygen has been widely studied in three main regions; the Herzberg

continuum (242 – 200) nm,^{4–9} the Schumann-Runge bands (200 – 176) nm^{10,11} and the Schumann-Runge continuum (176 – 100) nm.^{12–18} The electronic structure of molecular oxygen is complex with, for example, two ground state oxygen atoms giving rise to 81 possible molecular states,⁵ resulting in often complicated dissociation dynamics. However, the numerous theoretical and experimental studies, which have mainly focused on measuring the angular momentum alignment of the atomic photofragments and the spin-orbit branching ratios within the ground state O(3P_j) atoms, have enabled a good understanding of the dissociation dynamics involved in each of these bands, with multiple non-adiabatic transitions being found to occur.² These studies are all of dissociation following one-photon electric-dipole allowed transitions from the ground X $^3\Sigma_g^-$ state of O₂ and therefore probe the *ungerade* molecular states. In this work, two-photon absorption will be used to investigate the dissociation dynamics of the less widely studied *gerade* states of O₂.

The lowest energy molecular orbital configuration of O₂ is $...(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$, with the doubly occupied $1\pi_g$ orbital giving rise to the three lowest electronic states; X $^3\Sigma_g^-$, a $^1\Delta_g$ and b $^1\Sigma_g^+$. Removal of one $1\pi_g$ electron creates the X $^2\Pi_g$ state of O₂⁺ and the addition of a $n s\sigma_g$ Rydberg electron around this ion core forms the lowest-energy *gerade* Rydberg series of O₂; the $n s\sigma_g$ Rydberg series (principal quantum number $n = 3, 4, 5, \dots$). The lowest energy member of this series, the C $^3\Pi_g$ Rydberg state with $n = 3$, is the subject of this investigation. There have been many previous experimental and theoretical investigations of the C state,^{19–28} which is found to be considerably perturbed due to predissociation. Notably, van der Zande *et al.*²⁶ studied the dynamics of this predissociation process using kinetic energy release spectroscopy and concluded that the predissociation is caused by the 1 $^3\Pi_g$ valence state which crosses the C state at low vibrational levels. The principal molecular-orbital configuration of the 1 $^3\Pi_g$ valence state differs from the C Rydberg state by two orbitals, resulting in strong homogeneous Rydberg-valence interactions. The 1 $^3\Pi_g$ state correlates diabatically with the O(1D_2) + O(3P_j) limit, whilst an avoided crossing with the 2 $^3\Pi_g$ valence state would result in the adiabatic dissociation limit

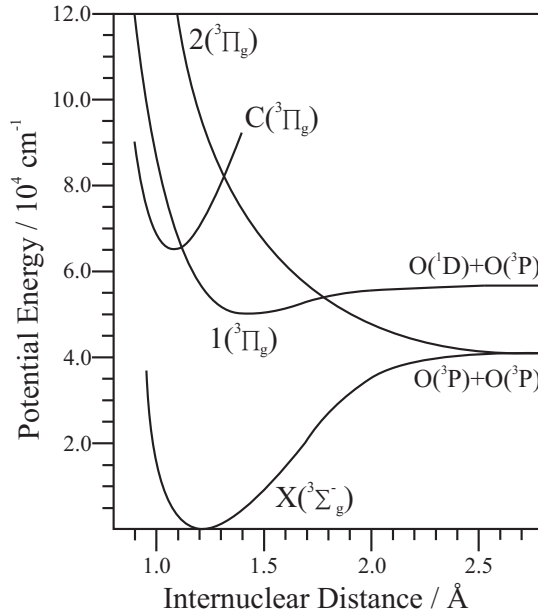


Figure 5.1: Schematic diagram of the relevant diabatic potential energy curves of O₂ adapted from Ref. 25.

being O(3P_j) + O(3P_j). It has been shown both theoretically²⁸ and experimentally²⁶ that the diabatic, O(1D_2) + O(3P_j) limit, is the major dissociation channel with, for example, Van der Zande *et al.*²⁶ measuring a 91% yield for this channel for predissociation from the C ($v = 0$) state. An approximate diabatic representation of the relevant potential energy curves, adapted from Ref. 25, is shown in figure 5.1 and is based on the valence states calculated by Saxon and Liu.²⁹

5.2 REMPI spectra

Firstly, (2+1) REMPI spectra of O₂ X $^3\Sigma_g^-$ excited *via* the C $^3\Pi_g$ ($v = 0$) and ($v = 1$) states in the wavelength regions (303.5 – 305.5) and (294.5 – 297.5) nm were recorded and are shown in figure 5.2. As expected, the spectra are broad and rotationally unresolved in agreement with previous REMPI measurements.^{20,22} A spectral simulation of both bands using the molecular constants of Sur *et al.*²⁰ assuming that the rotational constants for the C ($v = 0$) and ($v = 1$) states are the same as the rotationally resolved C ($v = 2$) state, and a rotational temperature

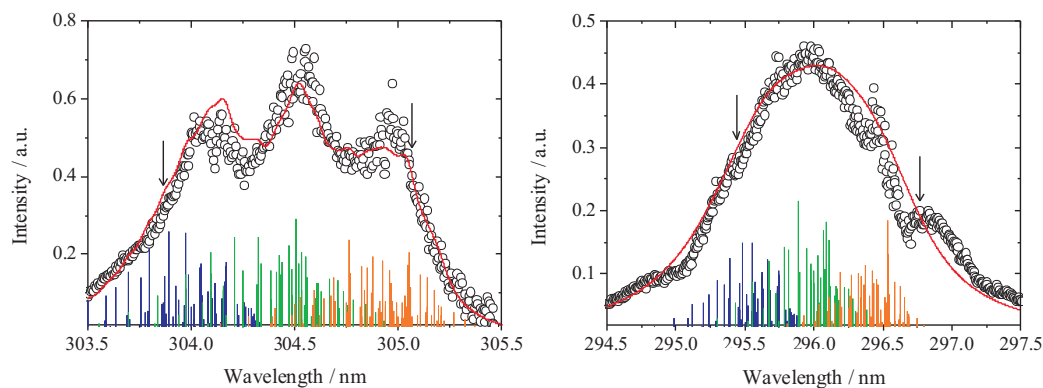


Figure 5.2: REMPI spectra of O₂ X $^3\Sigma_g^-$ excited *via* the C $^3\Pi_g$ ($v = 0$) (left) and ($v = 1$) (right) states. Open circles are the experimental data, whilst the solid line is the best-fit spectral simulation of the band. Solid lines show the line positions of the band with orange, green and blue lines representing the $|\Omega| = 0, 1$ and 2 states respectively.

of 140 K was generated using the PGopher spectral simulation program.³⁰ These are also shown in figure 5.2 along with the simulated line positions. The natural linewidth of the simulation was optimised to fit the experimental data returning a natural linewidth of $28 \pm 5 \text{ cm}^{-1}$ for C ($v = 0$) and $152 \pm 10 \text{ cm}^{-1}$ for C ($v = 1$) corresponding to excited state lifetimes of 0.19 and 0.03 ps respectively. This data is presented in table 5.1 along with previous experimental and theoretical determinations of the linewidths. There is clearly a wide variation in the previous experimental and theoretical measurements but the measurements presented here are generally in good agreement with the literature, particularly those of van der Zande *et al.*²⁶ who employed the complimentary technique of kinetic energy release spectroscopy.

The arrows on the REMPI spectra in figure 5.2 indicate the four wavelengths, 295.44, 296.77, 303.87 and 305.07 nm, where the translational anisotropy and angular momentum polarisation of both the O(3P_j) and O(1D_2) photofragments has been measured. It is clear from the simulated line positions that two-photon excitation at 295.44 nm and 303.87 nm occurs predominantly to the $|\Omega| = 2$ component of the C ($v = 1$) and ($v = 0$) bands respectively, whilst at 296.77 and 305.07 nm excitation is mainly to the $|\Omega| = 0$ component of the respective bands. These four wavelengths

were therefore chosen in order to see the effect of the initially excited vibrational state and spin-orbit component of the C state on the observed dissociation dynamics.

Table 5.1: Measured lifetime broadening parameters in cm⁻¹ for the C $^3\Pi_g$ $v = 0$ and $v = 1$ states together with previous experimental and theoretical values.

v	This Work	Previous studies							
		Experimental				Theoretical			
0	28 ± 5	44 ³¹	50 ²⁴	< 20 ²¹	28 ²⁶	23.5 ²³	20.7 ²⁴	51.3 ^{27a}	38 ^{28b}
1	152 ± 10	222 ³¹	320 ²⁴	—	150 ²⁶	109 ²³	115.0 ²⁴	214 ^{27a}	150 ^{28b}

^a Average over all $|\Omega|$ states for $J = 2$.

^b For $J = 1$.

5.3 Determining the photofragment angular momentum alignment following two-photon dissociation

Whilst there have been many previous studies of photofragment angular momentum polarisation following a one-photon dissociation, there have been relatively few studies of photofragment polarisation produced following multi-photon dissociations. Two-photon dissociation has been studied both experimentally and theoretically for a wide range of diatomic molecules including NO,^{32,33} CO³⁴ and HCl.^{35,36} These studies have all focused on the translational anisotropy of the resulting photofragments in order to determine the symmetries of both the final and intermediate states involved in the two-photon absorption process. The measured angular distribution of photofragments following dissociation *via* a N -photon excitation with linearly polarised light is found to deviate significantly from equation (1.2), with higher order terms contributing to the observed translational anisotropy, and the N -photon generalisation of this equation for the dissociation of an isotropic ensemble of molecules

within the axial-recoil approximation is given by,³⁷

$$I(\theta_\epsilon) = \frac{1}{4\pi} \left(1 + \sum_{n \geq 2}^{2N} \beta_n P_n(\cos \theta_\epsilon) \right), \quad (5.1)$$

where the sum is over even n and the coefficients β_n describe the translational anisotropy for a multi-photon dissociation. For the two-photon dissociation studied in this chapter, equation (5.1) is simplified so that,

$$I(\theta_\epsilon) = \frac{1}{4\pi} (1 + \beta_2 P_2(\cos \theta_\epsilon) + \beta_4 P_4(\cos \theta_\epsilon)), \quad (5.2)$$

where β_2 and β_4 are the two translational anisotropy parameters required to fully describe the scattering distribution. Dixon³⁷ has calculated the values of β_2 and β_4 for two-photon dissociation *via* near resonant intermediate states and for fast dissociation, where rotation of the molecule following absorption is negligible, β_2 and β_4 are equal to $5/7$ and $-12/7$ respectively for a $\Sigma \rightarrow \rightarrow \Pi$ excitation. This result is independent of the symmetry of the virtual intermediate state and is equivalent to a $\cos^2 \theta_\epsilon \sin^2 \theta_\epsilon$ photofragment distribution.

Whilst previous studies have only focused on the translational anisotropy of photofragments following two-photon dissociation, in this chapter the angular momentum polarisation of the atomic photofragments will be measured. In the previous chapter it was shown how the angular momentum polarisation of atomic photofragments produced following a one-photon dissociation may be modelled in terms of a polarisation parameter formalism developed by Rakitzis and Zare³⁸ and this formalism will now be extended to include photofragments resulting from a two-photon dissociation mechanism.

If the two-photon absorption occurs *via* a single absorption route to a single surface then the photofragment angular momentum polarisation may be expressed in terms of a set of molecular-frame polarisation parameters, $a_q^{(k)}$, and using equa-

tion (4.6) the detection probability, I_{det} , is therefore given by,

$$I_{\text{det}} = \sum_{k=0}^{2J} s_k(j) \sum_{q=-k}^k a_q^{(k)} C_q^k(\theta, \phi), \quad (5.3)$$

where, as described previously, θ and ϕ are the polar angles describing the probe polarisation vector, $\mathbf{e}_{\text{probe}}$, relative to the photofragment recoil velocity vector, $\mathbf{v}$, and $C_q^k(\theta, \phi)$ are the modified spherical harmonics.³⁹

The O(1D_2) photofragments were probed by (2+1) REMPI *via* two different intermediate states, 1F_3 and 1P_1 , at 203.8 and 205.4 nm respectively⁴⁰ and the line-strength factors, s_k , for these transitions are simply calculated using equations (4.8) and (4.9). The O(3P_j) photofragments were probed state-selectively by (2+1) REMPI transitions at 226.233, 226.059 and 225.656 nm for $j = 0, 1$ and 2 respectively.⁴ The calculation of the line-strength factors for these transitions is more complicated since two-photon transitions at these wavelengths occur to multiple j states, some of which are Q-branch transitions thus making equation (4.8) inappropriate for linearly polarised probe light. Van Vroonhoven *et. al.*⁶ have shown that the line-strength factors in this case may be calculated by assuming that two-photon excitation occurs only *via* the $2s^22p^33s \ ^3S^0$ intermediate state, for which experimental⁴¹ and theoretical⁴² studies have shown to contribute 97% of the total two-photon line-strength, so that the line-strength factor, P_k , may be given by,

$$P_k = \sum_m (-1)^{j_i-m} \sqrt{2k+1} \begin{pmatrix} j_i & k & j_i \\ -m & 0 & m \end{pmatrix} \begin{pmatrix} j_f & 1 & j_e \\ -m & 0 & m \end{pmatrix}^2 \begin{pmatrix} j_e & 1 & j_i \\ -m & 0 & m \end{pmatrix}^2, \quad (5.4)$$

where the total angular momentum of the intermediate state, j_e , is 1 for this single intermediate state model. Since the final j state is not resolved in the (2+1) REMPI detection these line-strength factors must be averaged over all these possible states, which is done using the branching ratios tabulated by Bischel *et. al.*⁴¹ As discussed in the previous chapter, these P_k values must subsequently be converted into the s_k factors required for the polarisation parameter formalism by using equation (4.9).

For circular polarised probe light, equation (4.8) is appropriate for the Q-branch transitions and is used in conjunction with equation (4.9) and the branching ratios tabulated by Bischel *et al.*⁴¹ to determine s_k (in this case). The ^{16}O photofragments probed in this work have no nuclear spin and therefore, unlike chlorine, hyperfine depolarisation will not affect any of the measurements and does not need to be corrected for. All line-strength factors required for probing oxygen atoms described in this chapter are summarised in table 5.2.

Table 5.2: The line-strength factors for the atomic oxygen photofragments probed in this work. Line-strength factors with odd k are given for left circular polarised light and for right circular polarised light the sign of these factors should be inverted.

Fragment	Wavelength / nm	Polarisation	Line-strength factor			
			s_1	s_2	s_3	s_4
O($^1\text{D}_2$)	203.8 (<i>via</i> $^1\text{F}_3$)	Linear	0	0.8163	0	−0.7347
		Circular	0	−0.8163	−0.8748	−0.1224
O($^1\text{D}_2$)	205.4 (<i>via</i> $^1\text{P}_1$)	Linear	0	−0.7143	0	−6.8571
		Circular	−2.0412	0.7143	0	−1.1429
O($^3\text{P}_2$)	225.656	Linear	0	−1	0	0
		Circular	−1.6330	0.2313	0.4666	0.1633
O($^3\text{P}_1$)	226.059	Linear	0	1	−	−
		Circular	−1	0	−	−

Equation (5.3) now needs to be renormalised so that it describes the angular momentum of photofragments relative to unpolarised photofragments with an isotropic angular distribution. This is achieved by multiplying by $I(\theta_\epsilon)$ and the distribution of photofragments in the molecular frame following a two-photon photolysis using linearly polarised light within the axial-recoil approximation is therefore given by,

$$I_{\text{tot}} = \left(1 + \beta_2 P_2(\cos \theta_\epsilon) + \beta_4 P_4(\cos \theta_\epsilon)\right) \left(1 + s_2 \left[a_0^{(2)} C_0^2(\theta) + 2a_2^{(2)} C_2^2(\theta) \cos 2\phi\right] + s_4 \left[a_0^{(4)} C_0^4(\theta) + 2a_2^{(4)} C_2^4(\theta) \cos 2\phi\right]\right), \quad (5.5)$$

where polarisation parameters up to $k = 4$ have been included as appropriate for

O(1D_2) and O(3P_2) photofragments. For O(3P_1) photofragments only the polarisation parameters up to $k = 2$ should be included and obviously for O(3P_0) photofragments no polarisation parameters should be included since they may not display angular momentum polarisation.

Equation (5.5) must then be transformed into the laboratory frame to compare with the observed experimental profiles. This transformation is achieved in the same way as described in the previous chapter by defining three sets of laboratory-frame angles, $(\theta_D, 0)$, (Θ, Φ) and (γ, χ) which define ϵ_{phot} , ϵ_{probe} and $\mathbf{v}$ respectively relative to the laboratory z -axis, which is defined to be the TOF axis, and relating these to the molecular-frame angles θ_ϵ , θ and ϕ using equations (4.12 – 4.14). In order to simplify the laboratory frame transformation, the $a_2^{(k)}$ terms appearing in equation (5.5) were analysed assuming that the translational anisotropy is in the fast dissociation limit, with $\beta_2 = 5/7$ and $\beta_4 = -12/7$, so that equation (5.5) becomes,

$$I_{\text{tot}} = \left(1 + \beta_2 P_2(\cos \theta_\epsilon) + \beta_4 P_4(\cos \theta_\epsilon)\right) \left(1 + s_2 a_0^{(2)} C_0^2(\theta) + s_4 a_0^{(4)} C_0^4(\theta)\right) + 15 \cos^2 \theta_\epsilon \sin^2 \theta_\epsilon \left(s_2 a_2^{(2)} C_2^2(\theta) + s_4 a_2^{(4)} C_2^4(\theta)\right) \cos 2\phi. \quad (5.6)$$

This assumption ensures that the $\sin \theta_\epsilon$ term appearing in the denominator of equation (4.14) is cancelled when performing the reference frame transformation. As a consequence of this, the measured $a_2^{(k)}$ values will be affected by rotational depolarisation due to the finite lifetime of the dissociative state and this effect will be discussed in more detail later.^{43,44} The measured $a_0^{(k)}$ parameters, however, were fit using experimentally measured translational anisotropy parameters, making no assumptions on the excited state lifetime. As a consequence, these parameters will be independent of any lifetime depolarisation effects.

In order to determine the translational anisotropy and angular momentum polarisation parameters, TOF profiles were taken in geometry pairs G_1 , G_3 and G_4 . The expressions for the measured TOF profiles in these geometry pairs is determined using the method outlined above and substituting in the relevant laboratory-frame

angles so that the expression for the TOF profile is given in the form,

$$I = g_0 + g_2P_2(x) + g_4P_4(x) + g_6P_6(x) + g_8P_8(x), \quad (5.7)$$

where $P_k(x)$ are Legendre polynomials in terms of the fractional velocity component $x = \cos \gamma$. g_k are coefficients which will depend on the probe transition sensitivity factors, s_k , the translational anisotropy parameters, β_2 and β_4 , and the polarisation parameters, a_q^k . These will be unique for each experimental geometry defined by the laboratory frame angles θ_D , Θ and Φ . Note how, in contrast to equation (4.15), the expression for the TOF profile now includes higher-order Legendre polynomials and this is a consequence of the dissociation now being a two-photon process. The complete expressions calculated using this method are given in appendix B.

The experimental parameters describing core extraction and the temporal width of the probe laser were determined from best fits to TOF profiles of the O(3P_0) photofragments which can have no angular momentum alignment. Core extraction will depend on the velocity of the photofragment and will therefore be the same for each photofragment at the same dissociation wavelength and the values determined for O(3P_0) are therefore used for all of the photofragments. Translational anisotropy parameters were determined by fitting to profiles taken in geometry pair G_3 , whilst alignment parameters were determined by fitting to profiles taken in geometry pair G_4 . The starting point for fitting the profiles taken in these geometry pairs at each dissociation wavelength was to determine the translational anisotropy parameters for the O(3P_0) photofragments. These values of β_2 and β_4 were then used to fit the TOF profiles taken in geometry pair G_4 for all other photofragments to determine the polarisation parameters. Profiles taken in geometry pair G_3 were then fit using the polarisation parameters determined from the previous fit to obtain β_2 and β_4 for the specific photofragment. This process was repeated until there was no improvement in the fits for either geometry pair.

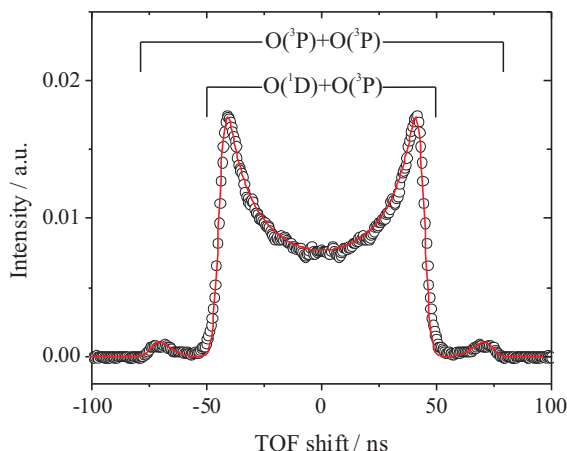


Figure 5.3: Sample experimental (open circles) and simulated (solid line) profile for $O(^3P_2)$ photofragments produced following two-photon dissociation at 303.87 nm, recorded in geometry G_1 .

5.4 $O(^3P_j)$ photofragment branching ratios

Firstly, profiles of $O(^3P_j)$ atoms were taken in geometry G_1 for the four wavelengths indicated in figure 5.2. The TOF profile for $O(^3P_2)$ following dissociation at 303.87 nm is shown in figure 5.3 along with a fitted simulation of the profile. There is clear evidence of two energetically accessible dissociation limits with the faster channel corresponding to the $O(^3P_j) + O(^3P_j)$ limit, where the energy release corresponds to the well-known bond dissociation energy, D_0 , for O_2 of 5.117 eV.⁴⁰ The slower, more intense channel corresponds to the $O(^1D_2) + O(^3P_j)$ limit, with the lower energy release reflecting the extra 1.967 eV required to produce electronically excited oxygen atoms. The resolution of the experiment is insufficient to distinguish between $O(^1D_2)$ produced in conjunction with the different $O(^3P_{j=0,1,2})$ spin-orbit states.

Integration of the measured signal intensities for $O(^3P_{j=0,1,2})$ for both channels yields a value for the branching ratio, $I/(I + II)$, where I and II correspond to the $O(^3P_j) + O(^3P_j)$ and $O(^1D_2) + O(^3P_j)$ limits respectively, of 0.03 ± 0.005 for all photolysis wavelengths and is consistent with a predominantly diabatic dissoci-

ation along the 1 $^3\Pi_g$ valence state. This measured branching ratio is somewhat smaller than the values of 0.08 and 0.07 measured by van der Zande *et al.*²⁶ for the C ($v = 0$) and ($v = 1$) bands respectively and 0.09 theoretically predicted by the coupled-channel Schroedinger equation model of Morrill *et al.*²⁸ The value measured from our TOF profiles is, however, expected to be an underestimate of the true branching ratio since core extraction effects will be more significant for the faster O(3P_j) + O(3P_j) channel than the slower O(1D_2) + O(3P_j) channel. From the simulated degree of core extraction for each dissociation channel, the branching ratio in the absence of core extraction effects is estimated to be 0.1 ± 0.05 , in good agreement with the literature values.

Table 5.3: Measured O(3P_j) spin-orbit branching ratios for the O(1D_2) + O(3P_j) channel.

O(3P_j) state	C ($v = 0$)		C ($v = 1$)	
	303.87 nm	305.07 nm	295.44 nm	296.77 nm
	$ \Omega = 2$	$ \Omega = 0$	$ \Omega = 2$	$ \Omega = 0$
$j = 2$	0.68 ± 0.05	0.43 ± 0.07	0.53 ± 0.02	0.49 ± 0.08
$j = 1$	0.28 ± 0.04	0.39 ± 0.05	0.41 ± 0.05	0.42 ± 0.04
$j = 0$	0.05 ± 0.02	0.18 ± 0.06	0.06 ± 0.01	0.09 ± 0.02

Integration of the measured O($^3P_{j=0,1,2}$) profiles taken in geometry G_1 for the O(1D_2) + O(3P_j) dissociation channel at each wavelength yields the spin-orbit branching ratio. These are shown in table 5.3 and are found to vary significantly with both vibrational excitation and Ω state probed. The branching ratios for the C ($v = 0$) state are found to be very dependent on the initially excited Ω state, with both ratios a long way from the statistical limit (5 : 3 : 1). The C ($v = 1$) state, however, shows much less variation with dissociation wavelength and the branching ratios are found to be much closer to the statistical limit. The determination of accurate spin-orbit branching ratios from REMPI spectra is non-trivial and efforts were made to ensure overlap of the counter-propagating beams was maximised for all experimental measurements. In addition, the probe laser power was varied to

verify that none of the transitions were being saturated. The errors represent twice the standard deviation of values from five separate measurements.

5.5 Translational anisotropy

Translational anisotropy parameters for the O(1D_2) + O(3P_j) channel were determined by fitting simulations to the sum and difference of TOF profiles taken in geometry pair G_3 . Sample data and fits for O(3P_2) produced following two-photon dissociation at 305.07 nm and O(1D_2) produced following two-photon dissociation at 296.77 nm are shown in figures 5.4 and 5.5 respectively. The fits are generally very good with the slightly worse fits for O(1D_2) reflecting the fact that profiles recorded by probing O(1D_2) *via* both the 1F_3 and 1P_2 intermediates have been fit simultaneously. The measured anisotropy parameters, β_2 and β_4 , for both O(3P_j) and O(1D_2) products are shown in table 5.4, with the observed values at each wavelength showing excellent agreement regardless of the photofragment probed. There is a small but significant difference between the different dissociation wavelengths within the same band, whilst the most noticeable difference is that the translational anisotropy parameters for predissociation from C ($v = 0$) are much smaller than from C ($v = 1$).

For rapid dissociation following a $\Sigma \rightarrow \rightarrow \Pi$ transition, the translational anisotropy parameters, β_2 and β_4 , are given by 5/7 and $-12/7$ respectively. A reduction in the measured anisotropy from these limiting values may either be caused by a competing transition to an excited state of different symmetry or by the excited state having a long lifetime prior to dissociation. Firstly, the possibility of absorption to excited states of different symmetries will be considered. Inspection of the potential energy curves for O₂ shows that there are no other two-photon electric-dipole allowed transitions close to the two-photon energies used in this work²⁹ and therefore any contributions from a different dissociative state must therefore be very small

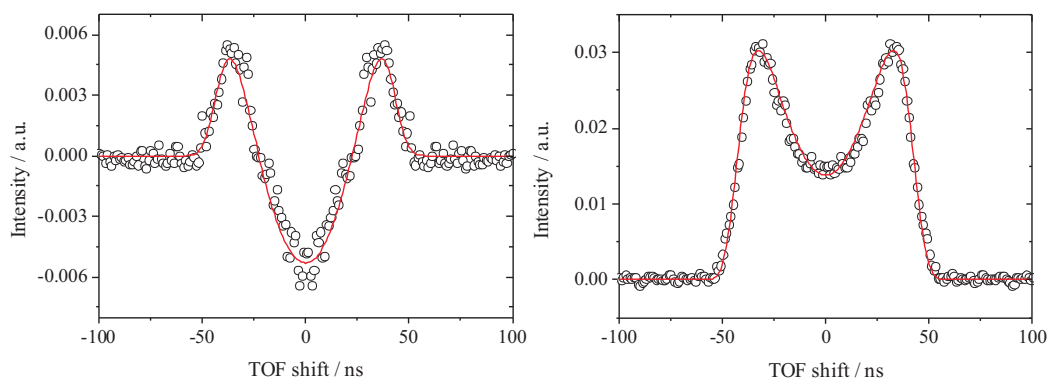


Figure 5.4: Sample experimental (open circles) and simulated (solid line) sum (right) and difference (left) profiles used to extract the translational anisotropy parameters following two-photon dissociation at 305.07 nm for the O(3P_2) photofragments.

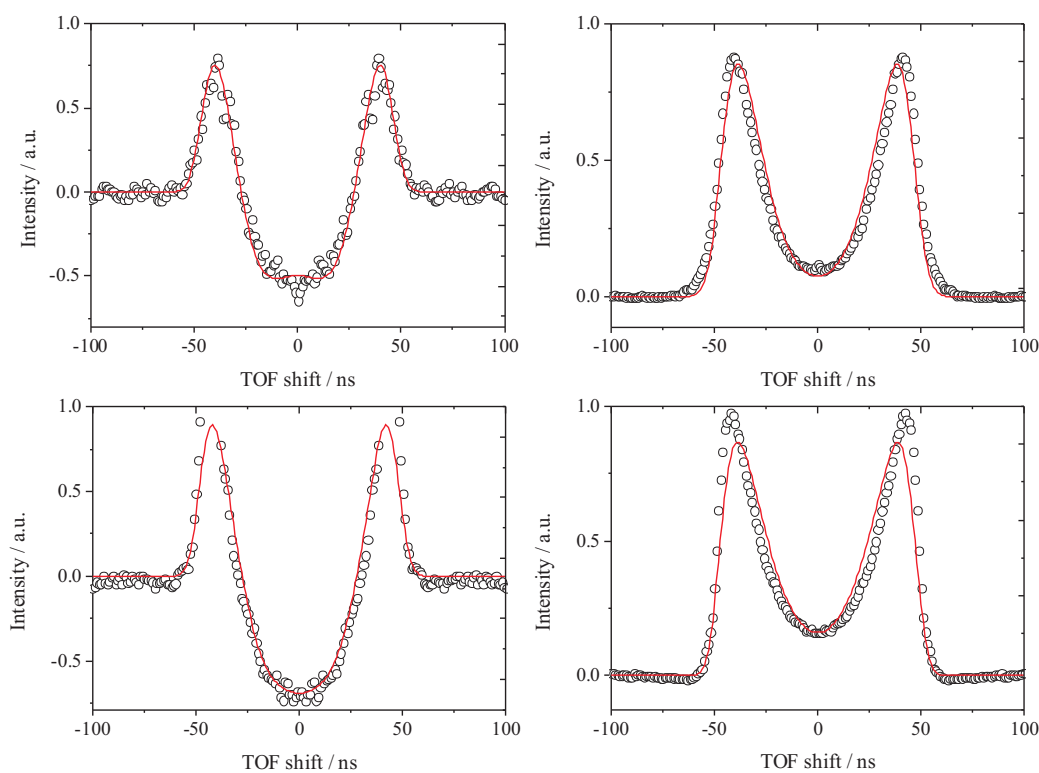


Figure 5.5: Sample experimental (open circles) and simulated (solid line) sum (right) and difference (left) profiles used to extract the translational anisotropy parameters following two-photon dissociation at 296.77 nm for the O(1D_2) photofragments probed *via* the 1F_3 (top) and 1P_2 (bottom) intermediates.

Table 5.4: Measured translational anisotropy parameters for all photofragments along with calculated translational anisotropy parameters assuming lifetime depolarisation from the limiting values of $\beta_2 = 5/7$ and $\beta_4 = -12/7$ using equations (5.9) and (5.10) as described in the text.

Fragment	Parameter	C ($v = 0$)		C ($v = 1$)	
		303.87 nm	305.07 nm	295.44 nm	296.77 nm
O(1D_2)	β_2	0.35 ± 0.12	0.45 ± 0.12	0.61 ± 0.10	0.65 ± 0.11
	β_4	-0.40 ± 0.17	-0.61 ± 0.16	-1.45 ± 0.17	-1.43 ± 0.15
O(3P_2)	β_2	0.25 ± 0.10	0.48 ± 0.10	0.6 ± 0.10	0.7 ± 0.10
	β_4	-0.45 ± 0.10	-0.75 ± 0.11	-1.45 ± 0.13	-1.45 ± 0.12
O(3P_1)	β_2	—	0.31 ± 0.10	0.62 ± 0.09	0.62 ± 0.10
	β_4	—	-0.68 ± 0.10	-1.44 ± 0.12	-1.42 ± 0.13
O(3P_0)	β_2	—	0.36 ± 0.10	0.67 ± 0.10	0.60 ± 0.10
	β_4	—	-0.72 ± 0.11	-1.47 ± 0.15	-1.54 ± 0.11
	$\beta_2(\text{calc})$	0.29	0.41	0.67	0.68
	$\beta_4(\text{calc})$	-0.41	-0.62	-1.41	-1.50

and could not result in the observed reductions seen in this work. For a molecule purely described by Hund's case (a), the projection of the molecule's total spin on the internuclear axis, Σ , is well defined and the $\Delta\Sigma = 0$ selection rule⁴⁵ dictates that for a $\Sigma \rightarrow \rightarrow \Pi$ transition $\beta_2 = 5/7$ and $\beta_4 = -12/7$. If, however, the molecule has some Hund's case (c) character, Σ becomes less well defined and two-photon absorption steps of different symmetries may contribute to the overall absorption process and may cause a reduction in the observed translational anisotropy. The appropriate Hund's case for a molecule is determined by the ratio of its spin-orbit splitting energy, A , to the exchange energy, K , and if $A/K \ll 1$ Hund's case (a) holds rigorously. Using the average spin-orbit splitting of 97 cm^{-1} determined by Sur *et al.*²⁰ together with the exchange energy of $41 \pm 2 \text{ meV}$ determined by van der Zande *et al.*²⁶ A/K is found to be 0.29 and therefore the C state is predominantly case (a) in character but will have significant case (c) character. Therefore the total electronic angular momentum projection quantum number, Ω , is well defined but Σ is less well defined and so two-photon absorptions of different symmetries may contribute to the overall absorption to the C state.

To determine how this mixed case (a)/(c) character may affect the overall measured translational anisotropy, the symmetries of the possible intermediate and final states must be considered. At the one-photon energies used in this work, there are only two nearby valence states which may be accessed by a fully allowed electric-dipole transition from the ground X $^3\Sigma_g^-$ state of O₂; the B $^3\Sigma_u^-$ and 1 $^3\Pi_u$ states.²⁹ These play a prominent role in the dipole-forbidden Herzberg transitions, which lie in the wavelength region (240 – 300) nm,⁴ and it is therefore likely that these states will also be important at the very similar one-photon wavelengths used in this work. By weighting the contributions from each state by their energy mismatch, calculated using the valence states given in Ref. 29, and using theoretically determined values for the transition moments from X $^3\Sigma_g^-$ to the B $^3\Sigma_u^-$ and 1 $^3\Pi_u$ states,⁴⁶ the relative contribution of these two states to the virtual intermediate state of the two-photon absorption process may be estimated to be 99.7% B $^3\Sigma_u^-$ for all one-photon wavelengths. In addition, the states accessed in the electric-dipole forbidden $b \leftarrow X$ and $A \leftarrow X$ transitions, which occur in the near visible and UV and may also contribute to the virtual intermediate state, are also Σ states.

As described previously, the wavelengths chosen in this work correspond to excitation of predominantly the $|\Omega| = 0$ and 2 components of the C ($v = 0$) and ($v = 1$) states and, if the $\Delta\Sigma = 0$ selection rule holds, absorption to these states must proceed *via* the pathway,

$$X \ ^3\Sigma_{g,\pm 1}^- \xrightarrow{\mu_{\parallel}} \Sigma_{\pm 1} \xrightarrow{\mu_{\perp}} C \ ^3\Pi_{g,0,\pm 2}, \quad (5.8)$$

where we assume that the intermediate virtual state has only Σ character. This corresponds to a parallel ($\Delta\Omega = 0$) followed by a perpendicular ($\Delta\Omega = \pm 1$) transition, with dipole moments labelled as $\mu_{\parallel}$ and $\mu_{\perp}$ respectively, and will correspond to translational anisotropy parameters of $\beta_2 = 5/7$ and $\beta_4 = -12/7$ as mentioned previously. If, however, this $\Delta\Sigma = 0$ selection rule is relaxed then transitions with different $\Delta\Omega$ values may occur between the X and C state, resulting in a reduced translational anisotropy.

The large reduction in the measured translational anisotropy from the expected limiting values is, however, most likely to be due to the long lifetime of the pre-dissociated C state. There have been many studies of translational anisotropy as a function of excited state lifetime for both one and two-photon excitations.^{32,47} The measured REMPI spectra in this work are not rotationally resolved and hence the quantum mechanical treatment used in those previous studies is not applicable. Instead, the quasiclassical approach of Ref. 37 will be used to model the reduction in the observed translational anisotropy due to the long lifetime of the excited state. This approach assumes an exponentially decaying distribution of post excitation angles, γ , through which the molecule has rotated in the time between initial photon absorption and dissociation. Each anisotropy parameter will consequently become attenuated by a factor, $\langle P_0^k(\cos \gamma) \rangle$, which, when normalised to $\langle P_0^0(\cos \gamma) \rangle = 1$, are given by,³⁷

$$\langle P_0^2(\cos \gamma) \rangle = \frac{1}{4} \left(\frac{3}{4y^2 + 1} + 1 \right), \quad (5.9)$$

$$\langle P_0^4(\cos \gamma) \rangle = \frac{1}{64} \left(\frac{35}{16y^2 + 1} + \frac{20}{4y^2 + 1} + 9 \right), \quad (5.10)$$

where $y \equiv 2B|\mathbf{J}|/\Gamma$ and is equal to the ratio of angular frequency to decay time constant, where $|\mathbf{J}| = \sqrt{J(J+1) - \Lambda^2}$, B is the molecular rotational constant, Γ is the homogeneous linewidth and Λ is the molecular frame electronic orbital angular momentum projection quantum number along the inter-nuclear axis. It has been shown numerically by Dixon³⁷ that translational anisotropy parameters calculated in this way represent a weighted mean of the translational anisotropy parameters over the entire spectral band.

The calculated translational anisotropy parameters using equations 5.9 and 5.10, assuming that depolarisation is from the limiting values of 5/7 and $-12/7$ are shown in table 5.4. Here the fitted values for the lifetime broadening, Γ , are used together with an average J determined from the spectral simulations of 7.6, 4.4, 6.6 and 5.2 for dissociation at 303.87, 305.07, 295.44 and 296.77 nm respectively. The agreement between the calculated and measured anisotropy is in general very good, with

variations in J causing the small observed variations within the same band and different lifetime broadening parameters causing the large variation between the two bands. This analysis is clearly subject to many approximations but does show, at least qualitatively, that the difference in anisotropy parameters at the different wavelengths can be attributed to lifetime depolarisation effects and that the values of β_2 and β_4 in the absence of this depolarisation must be close to $5/7$ and $-12/7$. The data therefore suggests that mixed transitions of different symmetries make a very small contribution to the overall two-photon absorption and justifies the use of a single surface dissociation model to describe the photofragment angular momentum alignment.

5.6 Angular momentum alignment

Polarisation parameters for both O($^3P_{j=2,1}$) and O(1D_2) photofragments produced *via* the O(1D_2) + O(3P_j) channel were determined by fitting simulations to the sum and difference of TOF profiles taken in geometry pair G_4 . Sample data and fits for O(3P_2) fragments produced following two-photon dissociation at 295.44 nm and O(1D_2) produced following two-photon dissociation at 296.77 nm are shown in figures 5.6 and 5.7 respectively.

The measured alignment parameters are shown in table 5.5 and in all cases only the $a_0^{(k)}$ parameters, where $k = 2$ for O($^3P_{j=2,1}$) and $k = 2, 4$ for O(1D_2), were observed. The absence of $k = 4$ alignment parameters for the O($^3P_{j=2}$) photofragments is due to the line-strength factor, s_4 , being zero, as shown in table 5.2. There was no evidence for non-zero values of the $a_2^{(k)}$ parameters for any of the photofragments or dissociation wavelengths. These parameters result from coherent perpendicular excitation to degenerate $\pm\Omega$ states³⁸ and may therefore be non-zero for excitation to $|\Omega| = 2$ at 303.87 and 295.44 nm. Their absence at these wavelengths is possibly due to the effect of rotational depolarisation since, as mentioned in section 5.3, these parameters were fit assuming the fast recoil limit. Clearly, the measured translational anisotropy parameters show that the dissociation is not in the fast recoil limit and

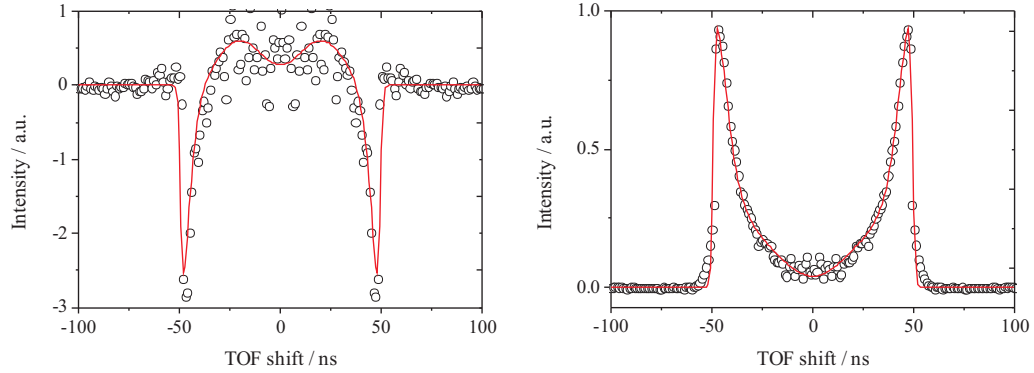


Figure 5.6: Sample experimental (open circles) and simulated (solid line) sum (right) and difference (left) profiles used to extract the polarisation parameters following two-photon dissociation at 295.44 nm for the O(3P_2) photofragments.

Table 5.5: Measured $a_0^{(k)}$ polarisation parameters for all photofragments.

Fragment	Parameter	C ($v = 0$)		C ($v = 1$)	
		303.87 nm $ \Omega = 2$	305.07 nm $ \Omega = 0$	295.44 nm $ \Omega = 2$	296.77 nm $ \Omega = 0$
O(1D_2)	$a_0^{(2)}$	-0.29 ± 0.09	-0.17 ± 0.12	-0.40 ± 0.15	-0.38 ± 0.14
	$a_0^{(4)}$	0.10 ± 0.03	0.03 ± 0.04	0.05 ± 0.03	0.03 ± 0.03
O(3P_2)	$a_0^{(2)}$	0.28 ± 0.08	0.1 ± 0.07	0.33 ± 0.06	0.03 ± 0.06
O(3P_1)	$a_0^{(2)}$	—	-0.24 ± 0.05	-0.04 ± 0.03	-0.24 ± 0.09

therefore the measured $a_2^{(k)}$ parameters will be reduced by a factor similar to that calculated in equation (4.26); the extension of equation (4.26) to include two-photon dissociations will be discussed in more detail later in the chapter when dealing with the orientation parameters.

The measured alignment at each dissociation wavelength is clearly different for each photofragment probed, with the measured O(1D_2) and O(3P_2) alignment being

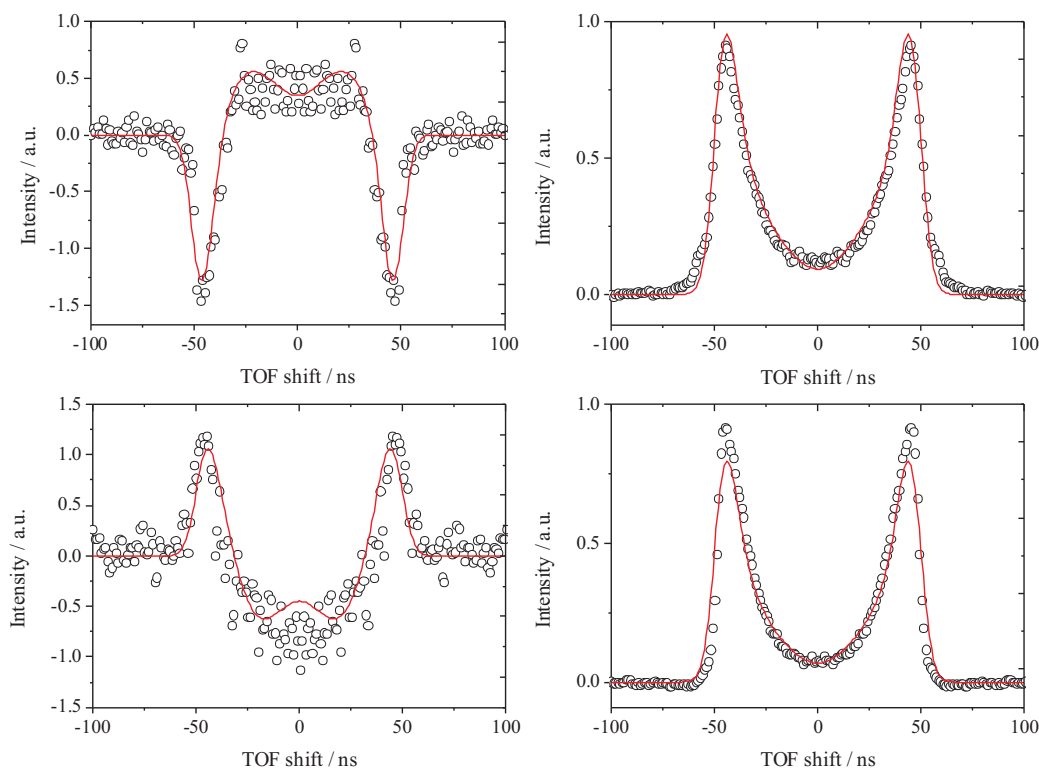


Figure 5.7: Sample experimental (open circles) and simulated (solid line) sum (right) and difference (left) profiles used to extract the polarisation parameters following two-photon dissociation at 296.77 nm for the O(1D_2) photofragments probed *via* the 1F_3 (top) and 1P_2 (bottom) intermediates.

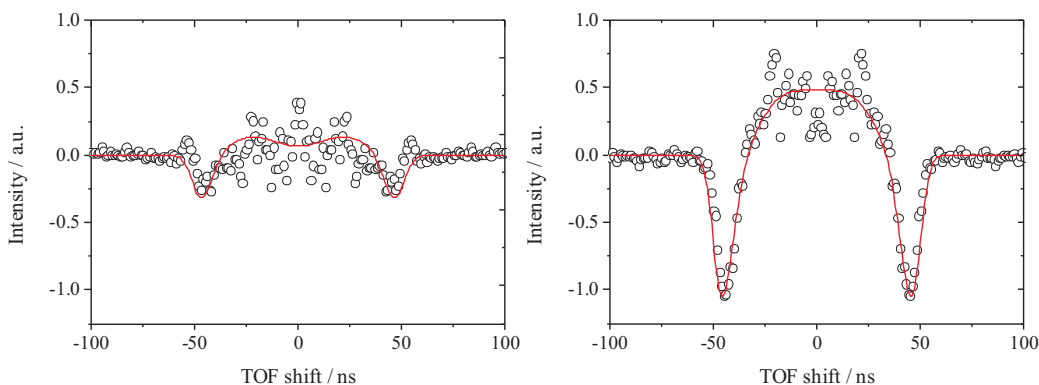


Figure 5.8: Experimental (open circles) and simulated (solid line) difference profiles taken in geometry pair G_4 for the O(3P_1) photofragments produced following two-photon dissociation at 295.44 (left) and 296.77 nm (right).

of opposite sign. In addition, the measured alignment for the O(3P_j) photofragment is clearly very sensitive to the initially excited Ω state, with O(3P_2) photofragments produced following absorption to the $|\Omega| = 0$ component of the C state clearly having a much smaller alignment than photofragments produced following absorption to the $|\Omega| = 2$ component and O(3P_1) photofragments showing the opposite trend. This difference in alignment due to the initially excited Ω state is clearly illustrated in figure 5.8, where difference profiles for the O(3P_1) photofragments taken in geometry pair G_4 are shown with the same scale for two-photon absorption at 295.44 ($|\Omega| = 2$) and 296.77 nm ($|\Omega| = 0$), with the difference profile for dissociation at 295.44 nm clearly having a much smaller amplitude.

It is also interesting to note that the O(3P_2) alignment is of opposite sign to that for O(3P_1). This has also been observed for N₂O photolysis⁴⁸ where dissociation was found to occur *via* a diabatic dissociation pathway. Unlike for O(3P_j), the O(1D_2) alignment is found to be constant for both dissociation wavelengths within the C ($v = 1$) band. Whilst there is some variation in the measured angular momentum polarisation for O(1D_2) with initially excited Ω state for the C ($v = 0$) band, it is much less marked than for the O(3P_j) photofragments.

5.7 Modelling the angular momentum alignment and spin-orbit branching ratios

The photofragment alignment and spin-orbit branching ratio results may be interpreted in terms of two simple limiting cases for evolution of the molecule to the atomic asymptotes. The first is the adiabatic limit, which assumes that the dissociating molecule moves slowly through the spin-orbit coupling region, so that as the atoms dissociate the coupling between the atomic orbital and atomic spin angular momentum becomes stronger than the coupling of atomic orbital angular momentum to the internuclear axis. In this limit, the dissociating molecular state is well described by Hund's case (c) with Ω conserved at all internuclear distances.

Conversely, in the “sudden-recoil” or diabatic limit the dissociating molecule moves through the spin-orbit coupling region very rapidly so that there is insufficient time for the electronic and spin angular momentum to recouple at large internuclear distances. In this limit, the repulsive states in the short range molecular regime, described by Hund’s case (a), are simply projected onto the atomic limits without accounting for electronic evolution during the course of recoil.⁴⁹ This limit is described as diabatic with respect to spin-orbit coupling since this is accounted for by the basis transformation from molecular to product atomic states.⁵

The adiabatic or diabatic character of a dissociation process may be quantified by the Massey parameter,⁵⁰

$$\xi = \frac{d\Delta E_{SO}}{\hbar v}, \quad (5.11)$$

where ΔE_{SO} is the atomic spin-orbit splitting, d is the characteristic recoil distance and v is the atomic recoil velocity. The distance, d , has been estimated to be about $3 a_0$ in Ref. 18 from inspection of the O₂ potential energy curves. The spin-orbit splittings for O(3P_j) atoms are 0.00852 eV and 0.01962 eV for $j = 0-1$ and $j = 1-2$ respectively.⁴⁰ This yields Massey parameter values ranging from 0.36 and 0.84 for two-photon dissociation at 295.44 to 0.41 and 0.94 for dissociation at 305.07 nm. If $\xi \ll 1$ diabatic dynamics are predicted, whilst if $\xi \gg 1$ adiabatic dynamics are predicted. In this case, however, the Massey criterion indicates that the dissociation should exhibit a mixture of adiabatic and diabatic dynamics, which has previously been observed for the one-photon dissociation studies of O₂ at similar energies within the Schumann-Runge continuum.^{12-14,17,18}

5.7.1 Adiabatic model

In the adiabatic limit, the non-crossing rule applies to wavefunctions with the same value of Ω and therefore the energy ordering of Hund’s case (c) molecular states at short range will be maintained until dissociation. This means that spin-orbit branching ratios can be predicted using a Hund’s case (c) correlation diagram, whereby molecular case (c) states are matched directly to product atomic states. For light-

atom molecules, the spin-orbit coupling is weak and short-range curve crossings only carry a small probability of showing adiabatic behaviour.¹¹ This is demonstrated by the short-range crossing of the 2 $^3\Pi_g$ and 1 $^3\Pi_g$ valence states behaving predominantly diabatically and favouring the O(1D_2) + O(3P_j) dissociation limit. At longer range, the potential energy curves will be nearly parallel and hence the probability of an avoided crossing, and adiabatic dissociation occurring, is much higher. A correlation diagram for the *gerade* states associated with the O(1D_2) + O(3P_j) atomic limit can be drawn using the adiabatic correlation rules of Mulliken,⁵¹ whereby the non-crossing rule applies to wavefunctions with the same value of Ω . The energy ordering of states is determined from Ref. 29 for an internuclear distance, R , of 4.5 a_0 and the resulting adiabatic correlation diagram, assuming that all curve crossings occurring at longer internuclear distances behave adiabatically, is shown in figure 5.9. From this figure it is clear that adiabatic dissociation along the 1 $^3\Pi_g$ valence state correlates solely with O(3P_2) atomic products, in poor agreement with the experimental measurements. The internuclear distance from which the dissociation is assumed to proceed adiabatically is somewhat arbitrary and changing this will lead to a slightly different energy ordering of the valence states. Regardless of this choice of internuclear distance, the 1 $^3\Pi_g$ valence is always predicted to correlate solely with O(3P_2) atomic products using the adiabatic model.

The quadrupole-quadrupole interaction is found to be the dominant electrostatic interaction at long range and therefore, as with the dissociation of Cl₂ described in the previous chapter, the adiabatic wavefunctions may be determined by minimising this interaction.^{5,18} The required wavefunctions have been tabulated by Alexander⁵² and the dissociating wavefunctions adiabatically correlating to the case (c) molecular states resulting from the 1 $^3\Pi_g$ valence state may be determined from figure 5.9 and are found to be,

$$\Psi_{\text{elec}}^{\Omega=\pm 2} \xrightarrow{R \rightarrow \infty} 0.28098 (|\pm 2, 0\rangle + |0, \pm 2\rangle) - 0.91766 |\pm 1, \pm 1\rangle, \quad (5.12)$$

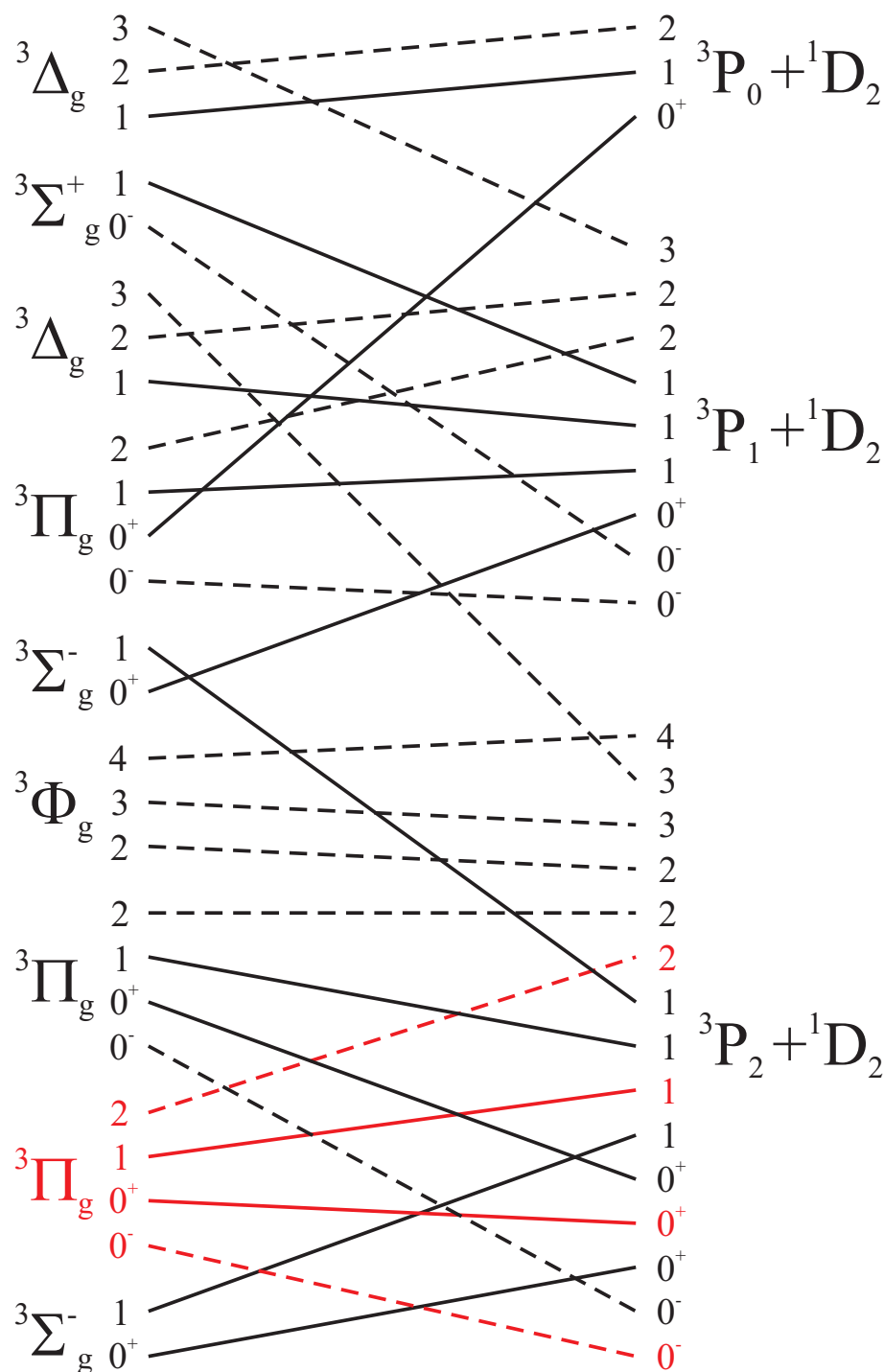


Figure 5.9: Adiabatic correlation diagram between Hund's case (c) molecular states and product atomic states with the energy ordering determined from Ref. 29 as described in the text. The numbers next to each level are the projection of the total angular momentum, Ω , and, for clarity, solid lines link levels with $\Omega = 0^+$ and 1, whilst all other levels are linked by dashed lines. The $1\ ^3\Pi_g$ valence state, on which dissociation takes place, is in red.

$$\Psi_{\text{elec}}^{\Omega=0^-} \xrightarrow{R \rightarrow \infty} 0.60150 (|\pm 2, \mp 2\rangle - |\mp 2, \pm 2\rangle) + 0.37175 (|\pm 1, \mp 1\rangle - |\mp 1, \pm 1\rangle), \quad (5.13)$$

$$\begin{aligned} \Psi_{\text{elec}}^{\Omega=0^+} \xrightarrow{R \rightarrow \infty} & 0.20636 (|\pm 2, \mp 2\rangle + |\mp 2, \pm 2\rangle) + 0.13159 (|\pm 1, \mp 1\rangle + |\mp 1, \pm 1\rangle) \\ & - 0.93819 |0, 0\rangle, \end{aligned} \quad (5.14)$$

where all terms are as defined in equation (4.27) except that the total electronic angular momentum states of the two atoms a and b , $|j_a, m_a\rangle|j_b, m_b\rangle$, have been shortened to $|m_a, m_b\rangle$ and $j_a = j_b = 2$ since the O(1D_2) and O(3P_2) photofragments. As described in the previous chapter, the square of the expansion coefficients will give the probability that an atomic photofragment will be in a state with a particular m_j value if dissociation proceeds adiabatically along each of these states and these calculated m_j populations may subsequently be converted into polarisation parameters using equation (4.29).

Within this limit, the incoherent $a_0^{(2)}$ polarisation parameter is calculated to be -0.421 for adiabatic dissociation along the $|\Omega| = 2$ spin-orbit component and -0.113 for adiabatic dissociation along the $|\Omega| = 0$ spin-orbit component for both O(1D_2) and O(3P_2) photofragments. Clearly, no predictions can be made for the alignment of the O(3P_1) photofragments using the adiabatic model since these fragments are not predicted to be produced. These calculations are in reasonable agreement with the measured O(1D_2) alignment parameters shown in table 5.5 but in complete disagreement with the measured alignment for the O(3P_2) photofragments. As mentioned previously, the choice of internuclear distance from which to assume that dissociation occurs adiabatically may affect the energy ordering of states but this will not change the main disagreement between the adiabatic model predictions and the measured results, which is that it predicts the same alignment for both O(1D_2) and O(3P_2) co-fragments, in clear disagreement with the measured results. The poor agreement with the measured spin-orbit branching ratios and angular momentum alignment to the predictions of the adiabatic model therefore suggests that the dissociation must be predominantly diabatic in character.

5.7.2 Diabatic model

In order to model the observed alignment and spin-orbit branching ratios the diabatic model developed by Singer *et al.*,⁵³ which has previously been applied to the dissociation of O₂, will be used.^{5,6,18} In the diabatic model the dissociating $^3\Pi_g$ molecular state is described by Hund's case (a) quantum numbers Λ , S and Σ corresponding to the molecular frame electronic orbital angular momentum projection along the inter-nuclear axis, total electronic spin and projection of the spin respectively. The two dissociating atoms will have total orbital angular momentum, l_i , and spin, s_i , where the subscript i labels the particular atom. In the diabatic "sudden-recoil" limit, spin-orbit coupling is neglected and therefore the projection of the atomic orbital angular momentum onto the internuclear axis, λ_i , for both atoms is defined by the projection of the molecular orbital angular momentum,

$$\Lambda = \lambda_{O(^3P)} + \lambda_{O(^1D)}. \quad (5.15)$$

Therefore, the possible atomic states correlating with the $\Lambda = \pm 1$ components of a molecular state are given by $|\lambda_{O(^1D)}\lambda_{O(^3P)}\rangle = |\pm 2, \mp 1\rangle, |\pm 1, 0\rangle, |0, \pm 1\rangle$. The correct combination of possible atomic states which correspond to the $1\ ^3\Pi_g$ molecular state upon which dissociation takes place now needs to be determined,

$$\Psi_{\pm 1} = c_1|\pm 2, \mp 1\rangle + c_2|\pm 1, 0\rangle + c_3|0, \pm 1\rangle. \quad (5.16)$$

Previous studies of O₂ dissociation have determined these wavefunctions by minimising the quadrupole-quadrupole interaction since, as mentioned previously, this is the electrostatic interaction which will dominate at long range.^{5,18} The matrix elements of the quadrupole-quadrupole operator, $\hat{V}^{(2,2)}(R)$, for two atomic fragments

a and b are given by,^{5,18}

$$\begin{aligned} \langle l_a \lambda'_a l_b \lambda'_b | \hat{V}^{(2,2)}(R) | l_a \lambda_a l_b \lambda_b \rangle = & (-1)^{l_a + l_b - \lambda'_a - \lambda'_b} \langle l_a || 2 || l_a \rangle \langle l_b || 2 || l_b \rangle \langle 2, m, 2, -m | 4, 0 \rangle \\ & \times \frac{70^{1/2}}{R^5} \begin{pmatrix} l_a & 2 & l_a \\ -\lambda'_a & m & \lambda_a \end{pmatrix} \begin{pmatrix} l_b & 2 & l_b \\ -\lambda'_b & -m & \lambda_b \end{pmatrix}, \end{aligned} \quad (5.17)$$

where $m = \lambda'_a - \lambda_a$, $\langle 2, m, 2, -m | 4, 0 \rangle$ is a Clebsch-Gordan coefficient³⁹ and $\langle l_x || 2 || l_x \rangle$ is the reduced quadrupole moment of the atom x . Since only the signs of these moments are required in the derivation, these may be calculated using a one-determinant approximation of the atomic wavefunction and for O(1D_2) and O(3P) atoms these reduced quadrupole moments are found to be,^{18,54}

$$\langle l_{O(^3P)} = 1 || 2 || l_{O(^3P)} \rangle = (6/5)^{1/2} \langle r^2 \rangle, \quad (5.18)$$

$$\langle l_{O(^1D)} = 2 || 2 || l_{O(^1D)} \rangle = -(14/5)^{1/2} \langle r^2 \rangle, \quad (5.19)$$

where $\langle r^2 \rangle$ is the expectation value of r^2 for an oxygen $2p$ orbital. The minimum quadrupolar-quadrupolar interaction energy is found variationally by solving the secular determinant for the wavefunction given in equation (5.16) and used to determine the corresponding values of c_1 , c_2 and c_3 which minimise this interaction. Using this method, it is found that values of $c_1 = 0.700$, $c_2 = 0.713$ and $c_3 = -0.037$ correspond to the minimum quadrupolar-quadrupolar interaction energy. The square of these coefficients will give the relative populations of the photofragment λ_i states and therefore populations of 0, 0.51 and 0.49 for $|\lambda_{O(^1D)}| = 0, 1$ and 2 respectively are predicted.

The projection of an atom's total angular momentum is simply described by its m_j populations which may be determined from the measured polarisation parameters, $a_0^{(k)}$, using equation (4.29). For the O(1D_2) photofragment the projection of its total angular momentum, m_j , is equal to the population of its λ_i states since it has no spin. Using equation (4.29) along with the measured alignment parameters

for the O(1D_2) photofragments for predissociation from the C ($v = 1$) state, where excitation energy is highest and dissociation should be closest to the diabatic limit, it is found that the measured alignment corresponds to a dissociating diabatic wavefunction with values for $|c_1|$, $|c_2|$ and $|c_3|$ of 0.452, 0.634 and 0.628 respectively. This correspond to populations of 0.39, 0.40 and 0.20 for $|m_j| = 0, 1$ and 2 respectively, in clear disagreement with the prediction obtained by minimising the energy of the quadrupolar-quadrupolar interaction.

Despite the lack of good agreement between these basic quantum mechanical calculations and experimentally determined O(1D_2) alignment parameters, the validity of the diabatic model may be tested by using the diabatic wavefunction inferred from the measured O(1D_2) alignment to predict the corresponding angular momentum alignment and spin-orbit branching ratios of the O(3P_j) co-fragments. To achieve this, the spin part of the molecular wavefunction in equation (5.16) should be included to give a molecular basis described by the quantum numbers $|\lambda_{O(^1D)}\lambda_{O(^3P)}S\Sigma; R\rangle$.⁵ The spin contribution, $|s\sigma\rangle$, for the O(3P_j) atom, where σ is the projection of the atomic spin, s , therefore needs to be included. Assuming Russell-Saunders coupling, the atomic states of O(3P_j) are given by,^{5,18}

$$|(ls)jm_j\rangle = \sum_{\lambda\sigma} |l\lambda\rangle |s\sigma\rangle \langle l\lambda s\sigma | jm_j\rangle, \quad (5.20)$$

where $\langle l\lambda s\sigma | jm_j\rangle$ is a Clebsch-Gordan coefficient. The probability, $P(j, m_j)$, of finding an O($^3P_{j=0,1,2}$) atom in a particular (j, m_j) atomic state is given by taking a weighted average of squared matrix elements describing the transformation between the atomic basis and the molecular wavefunctions over all relevant molecular spin state projections, Σ , for both diabatic wavefunctions, $\Psi_{\pm 1}$,

$$P(j, m_j) = \frac{1}{6} \sum_{\Sigma} \sum_{\lambda'_{O(^1D)}} |\langle jm_j l_{O(^1D)} \lambda'_{O(^1D)} | \Psi_{\pm 1} S \Sigma \rangle|^2, \quad (5.21)$$

Table 5.6: Calculated O(3P_j) spin-orbit branching ratios for the O(1D_2) + O(3P_j) channel using the diabatic and adiabatic models described in the text.

O(3P_j) state	Diabatic model		Adiabatic model	
	$ \Omega = 2$	$ \Omega = 0$	$ \Omega = 2$	$ \Omega = 0$
$j = 2$	0.63	0.47	1	1
$j = 1$	0.32	0.40	0	0
$j = 0$	0.05	0.13	0	0

where the transformation matrix elements are given by,¹⁸

$$\langle jm_j l_{O(^1D)} \lambda'_{O(^1D)} | \lambda_{O(^3P)} \lambda_{O(^1D)} S \Sigma \rangle = \delta_{\lambda'_{O(^1D)} \lambda_{O(^1D)}} \langle l_{O(^3P)} \lambda_{O(^3P)} s_{O(^3P)} \Sigma | jm_j \rangle. \quad (5.22)$$

For a homogeneous predissociation mechanism, the initially excited projection of the total angular momentum onto the molecular axis, Ω , will be conserved and therefore Σ is restricted so that $\Omega = \Sigma + \lambda_{O(^1D)} + \lambda_{O(^3P)}$. These populations can then be converted back into alignment parameters using equation (4.29). Spin-orbit branching ratios for O(3P_j) are found by summing these populations over all values of m_j for each for each individual j .

The predicted alignment and spin-orbit branching ratios for each O($^3P_{j=0,1,2}$) atom following dissociation from the $|\Omega| = 0$ and 2 components of the initially excited $^3\Pi_g$ molecular state are summarised in tables 5.7 and 5.6 respectively alongside the predictions from the adiabatic model described in the previous section. Generally, the diabatic model based on the measured O(1D_2) alignment predicts the observed atomic alignment and spin-orbit branching ratios of the O(3P_j) co-fragments very well, with the measured difference between the spin-orbit branching ratios and alignment for dissociation following initial excitation of $|\Omega| = 2$ and $|\Omega| = 0$ states being well reproduced. There is clearly much better agreement between the experimental measurements and predictions for the diabatic model rather than for the adiabatic dissociation model and therefore indicates that dissociation occurs predominantly *via* a diabatic mechanism. The most significant deviations from the

Table 5.7: Calculated values for the O($^3P_{j=2,1}$) photofragments using the diabatic and adiabatic models described in the text.

Fragment	Parameter	Diabatic model		Adiabatic model	
		$ \Omega = 2$	$ \Omega = 0$	$ \Omega = 2$	$ \Omega = 0$
O(3P_2)	$a_0^{(2)}$	0.41	0.08	-0.42	-0.11
O(3P_1)	$a_0^{(2)}$	-0.01	-0.24	—	—

diabatic predictions are for the O(3P_2) product alignment. This photofragment can be produced by an adiabatic dissociation mechanism and therefore deviations from the predicted alignment are likely to be due to the fact that dissociation is not completely in the pure diabatic limit and that there is some adiabatic character to the dissociation, as predicted earlier from the calculated Massey parameters. The measured alignment of O(1D_2) atoms produced *via* the C ($v = 0$) state shows some dependence on the initially excited Ω state, which is not predicted by a diabatic dissociation mechanism, and provides further evidence for the mixed diabatic/adiabatic nature of the dissociation.

5.8 Probing the angular momentum orientation

In addition to probing the atomic angular momentum alignment, TOF profiles were also taken in geometry pair G_5 , with the photolysis laser polarised at 45° to the TOF axis and the probe laser switched between left and right circular polarisation, at the same dissociation wavelengths for which the photofragment angular momentum alignment was determined. Raw experimental TOF profiles probing the O(1D_2) photofragment following two-photon dissociation at 303.87 nm are shown in figure 5.10, showing a clear difference between profiles taken with left and right circularly polarised probe light and therefore indicating that, in addition to being aligned, the photofragment angular momentum is oriented. This observed angular

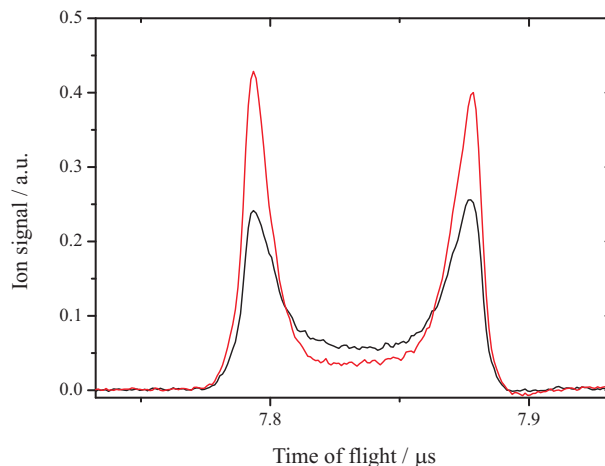


Figure 5.10: Raw experimental TOF profiles probing the O(1D_2) photofragment following two-photon dissociation at 303.87 nm, taken with the photolysis laser polarised at 45° to the TOF axis and a counter-propagating probe laser switched between left (black) and right (red) circular polarisation.

momentum orientation shows that, similar to a one-photon dissociation discussed in chapter 4, coherent orientation may also be observed for a two-photon dissociation process where transitions of different symmetries are involved.

5.8.1 Expressing photofragment orientation following a two-photon dissociation in terms of polarisation parameters

In this section the origin of the observed coherent orientation will be considered and it will be shown how, by making certain assumptions on the two-photon absorption process, the experimentally observed orientation may be simulated. The coherent orientation must be caused by interference between multiple coherently excited absorption routes and the possible absorption pathways which may cause this interference will now be considered. Firstly, two-photon absorption to the C $^3\Pi_{g,0,\pm 2}$ states may occur *via* intermediate states of different symmetry, *i.e.* Σ or Π . Interference between these dissociation pathways will not cause a polarisation interference since they will result in the same photofragment m_j distribution and will therefore lead

to an intensity interference effect and not a polarisation interference. Any observed photofragment orientation, *vide infra*, must therefore result from an absorption pathway to an excited state of different symmetry. In order for the dissociating pathways to interfere and cause the observed orientation, the two dissociation pathways must occur on the same timescale and, since the predissociation from C ($v = 0$) and ($v = 1$) states has been shown to have relatively long excited state lifetimes of 0.19 and 0.03 ps respectively, the observed orientation is unlikely to result from the simultaneous excitation of a nearby unbound valence state, which would be expected to have a much shorter lifetime. It is therefore concluded that the most likely cause of this interference is absorption pathways of different symmetries to the C state, which were discussed in section 5.5.

Whilst the wavelengths employed in this work will predominantly excite the $|\Omega| = 0$ or 2 components of the C ($v = 0$) and ($v = 1$) states, inspection of figure 5.2 shows that there will be a small but significant absorption to the $|\Omega| = 1$ component. Coherent orientation must result from transitions from the same ground state and, assuming that the intermediate state is still predominantly Σ in character, the most likely absorption pathway to cause the observed interference with the major absorption pathway given in equation (5.8) is,

$$X\ ^3\Sigma_{g,\pm 1}^- \xrightarrow{\mu_{\parallel}} \Sigma_{\pm 1} \xrightarrow{\mu_{\parallel}} C\ ^3\Pi_{g,\pm 1}. \quad (5.23)$$

For a pure Hund's case (a) molecule, the second one-photon transition of this absorption would be forbidden since it violates the $\Delta\Sigma = 0$ selection rule. As discussed in section 5.5, the C state has significant Hund's case (c) character and therefore Σ is less well defined and consequently this selection is relaxed so that the transition is not completely forbidden.

For a two-photon absorption process, the probability of absorbing two identical

photons of energy $h\nu$ is given by,³⁷

$$I_{\text{abs}} \propto \sum_e \left| \frac{\langle f | \boldsymbol{\mu} \cdot \mathbf{E} | e \rangle \langle e | \boldsymbol{\mu} \cdot \mathbf{E} | i \rangle}{(\Delta_e - h\nu + i(\Gamma_e/2))} \right|^2, \quad (5.24)$$

where the sum is over all the possible intermediate rovibronic states, e , separated from the ground state by energy Δ_e , and Γ_e is equal to the total homogeneous linewidth of the intermediate state. The denominator acts as a weighting factor for each of the possible intermediate states. If absorption occurs *via* an absorption pathway of a single symmetry, we can treat I_{abs} as the product of two one-photon transition moments and it is therefore proportional to $|\boldsymbol{\mu}_{fe} \cdot \mathbf{E}|^2 |\boldsymbol{\mu}_{ei} \cdot \mathbf{E}|^2$.

Coherent two-photon absorption *via* the absorption routes given in equations (5.8) and (5.23), which will be labelled A and B respectively with corresponding transition dipole moments $\boldsymbol{\mu}_A$ and $\boldsymbol{\mu}_B$, will now be considered. Using a similar analysis to that used by Rakitzis and Alexander⁵⁵ to describe dissociation *via* two dissociative states, the total transition dipole moment, $\boldsymbol{\mu}_{T_k}$, for each sequentially absorbed photon, k , is expressed as a weighted average of $\boldsymbol{\mu}_{A_k}$ and $\boldsymbol{\mu}_{B_k}$ given by $\boldsymbol{\mu}_{T_k} = c_A \boldsymbol{\mu}_{A_k} + c_B \boldsymbol{\mu}_{B_k}$. The total two-photon absorption probability, $|\boldsymbol{\mu}_{T_1} \cdot \mathbf{E}|^2 |\boldsymbol{\mu}_{T_2} \cdot \mathbf{E}|^2$, is now given by,

$$\begin{aligned} |\boldsymbol{\mu}_{T_1} \cdot \mathbf{E}|^2 |\boldsymbol{\mu}_{T_2} \cdot \mathbf{E}|^2 = & c_A^2 |\boldsymbol{\mu}_{\parallel} \cdot \mathbf{E}|^2 |\boldsymbol{\mu}_{\perp} \cdot \mathbf{E}|^2 + c_B^2 |\boldsymbol{\mu}_{\parallel} \cdot \mathbf{E}|^2 |\boldsymbol{\mu}_{\parallel} \cdot \mathbf{E}|^2 \\ & + 2c_A c_B (\boldsymbol{\mu}_{\parallel} \cdot \mathbf{E})(\boldsymbol{\mu}_{\perp} \cdot \mathbf{E}) |\boldsymbol{\mu}_{\parallel} \cdot \mathbf{E}|^2, \end{aligned} \quad (5.25)$$

where $c_A^2 + c_B^2 = 1$ since it is assumed that A and B are the only contributing pathways. I_{abs} now depends on two incoherent absorption probabilities multiplied by the probability that absorption occurs *via* each route, c_A^2 or c_B^2 , as well as an extra term which is due to a coherent absorption process occurring *via* both possible pathways.

The translational anisotropy of photofragments produced following a one-photon dissociation within the axial-recoil approximation is well known to be given by equation (1.2), where β is $+2$ for $|\boldsymbol{\mu}_{\parallel} \cdot \mathbf{E}|^2$ and -1 for $|\boldsymbol{\mu}_{\perp} \cdot \mathbf{E}|^2$, and substitution of this into equation (5.25) gives an expression for the angular distribution of photofrag-

ments, $I(\theta_\epsilon)$, following coherent two-photon absorption *via* both absorption routes A and B , which is found to be,

$$I(\theta_\epsilon) = \frac{1}{4\pi} \left(c_A^2 \left(1 + \frac{5}{7} P_2(\cos \theta_\epsilon) - \frac{12}{7} P_2(\cos \theta_\epsilon) \right) + c_B^2 \left(1 + \frac{20}{7} P_2(\cos \theta_\epsilon) + \frac{8}{7} P_2(\cos \theta_\epsilon) \right) + c_A c_B \frac{30}{\sqrt{2}} \cos^3 \theta_\epsilon \sin \theta_\epsilon \right), \quad (5.26)$$

where the two incoherent translational anisotropies are the same as would be calculated using equation (5.2) together with the values of β_2 and β_4 tabulated by Dixon.³⁷

As discussed in section 5.3, the effect of photofragment alignment on the TOF profile shape is determined by renormalising equation (5.3) so that it describes the angular momentum distribution of photofragments relative to unpolarised photofragments with an isotropic angular distribution. This is achieved by multiplying by the scattering angular distribution, $I(\theta_\epsilon)$, wherein the incoherent parts of equation (5.26) should be multiplied by the incoherent alignment parameters ($a_0^{(k)}$ and $a_2^{(k)}$ where k is even) as shown in equation (5.5), whilst the coherent term should be multiplied by the relevant coherent polarisation parameters. As discussed for one-photon dissociation, the interference between the parallel and perpendicular components of absorption of linearly polarised light is characterised by the coherent polarisation parameters, $\text{Im}[a_1^{(k)}]$, where k is odd, and $\text{Re}[a_1^{(k)}]$, where k is even.³⁸ By multiplying the incoherent and coherent parts of equation (5.26) by the relevant polarisation parameters and substituting in the one-photon translational anisotropies as described earlier, an expression for the recoil-frame detection probability within the axial-recoil approximation for dissociation following coherent two-photon absorption of linearly

polarised light *via* both absorption routes, I_{tot} , is determined. This is given by,

$$I_{\text{tot}} = c_A^2 I_{\text{tot},A}(\text{incoherent}) + c_B^2 I_{\text{tot},B}(\text{incoherent}) + \frac{30}{\sqrt{2}} \cos^3 \theta_\epsilon \sin \theta_\epsilon \left(\sum_{\text{odd } k}^{2j} s_k(j) \text{Im}[A_1^{(k)}] C_1^k(\theta) \sin \phi + \sum_{\text{even } k}^{2j} s_k(j) \text{Re}[A_1^{(k)}] C_1^k(\theta) \cos \phi \right), \quad (5.27)$$

where $\text{Im}[A_1^{(k)}] = c_A c_B \text{Im}[a_1^{(k)}]$ and $\text{Re}[A_1^{(k)}] = c_A c_B \text{Re}[a_1^{(k)}]$. $I_{\text{tot},A}(\text{incoherent})$ and $I_{\text{tot},B}(\text{incoherent})$ are given by equation (5.5) with the relevant values for β_2 and β_4 as given in equation (5.26) ($\beta_2 = 5/7$, $\beta_4 = -12/7$ for route A and $\beta_2 = 20/7$, $\beta_4 = 8/7$ for route B).

Equation (5.27) must now be transformed into the laboratory frame and integrated over all photofragments with the same velocity projection along the TOF axis to compare with the experimentally measured profiles.⁵⁶ This transformation is achieved by using the laboratory-frame angles defined in section 5.3 together with equations (4.12 – 4.14). For TOF profiles taken in geometry pair G_5 , with the photolysis laser polarised at 45° to the TOF axis and a counter-propagating probe laser switched between left and right circularly polarised light, then the laboratory-frame TOF profile, $I_{45\text{circ}}$, is found to be, ignoring higher order $k = 3$ terms,

$$I_{45\text{circ}} = I_{\text{tot},A}(\text{incoherent}) + s_1(j) \text{Im}[A_1^{(1)}] \left(\frac{45}{14} P_2(x) + \frac{15}{28} P_4(x) \right), \quad (5.28)$$

where $P_k(x)$ are Legendre polynomials of degree k in terms of the TOF shift, x and $I_{\text{tot},A}(\text{incoherent})$ is calculated using the method described in section 5.3 together with the previously measured polarisation parameters given in table 5.5. The full expression for the TOF profile, $I_{45\text{circ}}$, including the the incoherent alignment parameters is given in appendix B. As discussed in section 5.5, the measured translational parameters were measured to be close to limiting and any contributions from two-photon absorption steps of different symmetries must necessarily be very small and

$I_{\text{tot},B}(\text{incoherent})$ may therefore be ignored in the data analysis. $I_{\text{tot},A}(\text{incoherent})$ will be constant for both left and right circularly polarised probe light whilst the line-strength factor, $s_1(j)$, will change sign and therefore any difference in the TOF profiles for left and right circularly polarised probe light will be caused by non-zero values of the orientation parameter, $\text{Im}[A_1^{(1)}]$. This parameter may therefore be determined by simulating the difference between area normalised, symmetrised and baseline corrected TOF profiles recorded in geometry G_5 for left and right circularly polarised probe light using equation (5.28).

5.8.2 Results

Sample experimental difference profiles along with simulated best fits using equation (5.28) for the O(1D_2) and O(3P_2) co-fragments produced following two-photon dissociation at 295.44 and 303.87 nm are shown in figure 5.11. Difference profiles and best fits for the O(1D_2) and O(3P_1) co-fragments produced following two-photon dissociation at 296.77 and 305.07 nm are shown in figure 5.12. The simulated fits using equation (5.28) are generally very good, with the clear dip in the center of the profiles resulting from the higher order $P_0^4(x)$ term which is not present for one-photon dissociation.

The measured $\text{Im}[A_1^{(1)}]$ parameters for all photofragments are shown in table 5.8. For all measurements in table 5.8, the one-laser background signals, which were present for the REMPI schemes used to probe all the photofragments, were kept sufficiently low by reducing the probe laser power to ensure that they didn't affect the measured two-laser signals and could be successfully subtracted from the measured profiles. As shown in table 5.3, the O(3P_j) spin-orbit branching ratio varies significantly between the various two-photon dissociation wavelengths and the absence of O(3P_j) orientation results at particular wavelengths in table 5.8 is due to this change in spin-orbit branching ratios causing the two-laser signal for O(3P_j) atoms to be too low compared to the one-laser background signals to accurately measure the orientation at these wavelengths. For all results shown, the one-laser

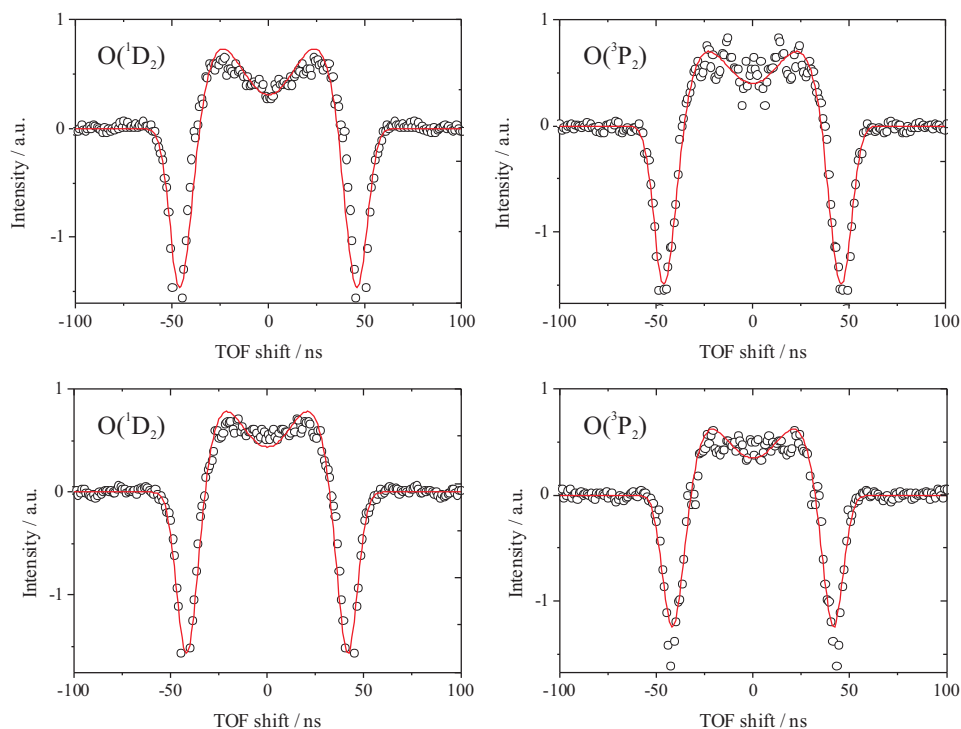


Figure 5.11: Sample symmetrised experimental (open circles) and simulated (solid line) difference profiles used to extract the orientation parameters following two-photon dissociation at 295.44 (top) and 303.87 nm (bottom) for the $O(^1D_2)$ (left) and $O(^3P_2)$ (right) photofragments.

background signals were minimised by keeping the probe laser power as low as possible and subtracted from the measured two-laser signals to yield the true pump-probe signal.

The measured $\text{Im}[A_1^{(1)}]$ parameters are in good agreement for the $O(^1D_2)$ and $O(^3P_2)$ co-fragments, with the consistently lower $O(^3P_1)$ orientation reflecting its lower value of j . All photofragments display the same general trend in measured orientation, with orientation resulting from predissociation *via* the $C(v=0)$ state generally lower than *via* $C(v=1)$. This trend is similar to that observed for the translational anisotropy parameters shown in table 5.4 measured at the same two-photon dissociation wavelengths. A similar rotational depolarisation may be

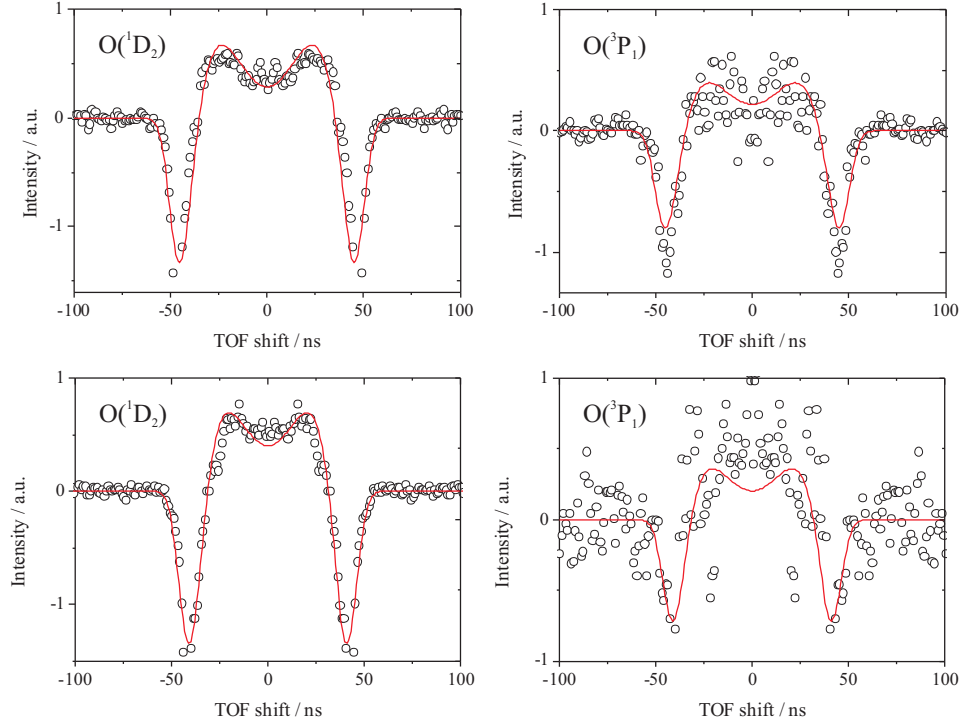


Figure 5.12: Sample symmetrised experimental (open circles) and simulated (solid line) difference profiles used to extract the orientation parameters following two-photon dissociation at 296.77 (top) and 305.07 nm (bottom) for the O(1D_2) (left) and O(3P_1) (right) photofragments.

Table 5.8: Measured orientation $\text{Im}[A_1^{(1)}]$ parameters for all photofragments resulting from the predissociation of the C ($v = 0$) and ($v = 1$) Rydberg states following two-photon absorption at various wavelengths.

Fragment	C ($v = 0$)		C ($v = 1$)	
	303.87 nm	305.07 nm	295.44 nm	296.77 nm
O(1D_2)	0.05 ± 0.02	0.08 ± 0.03	0.10 ± 0.03	0.10 ± 0.03
O(3P_2)	0.05 ± 0.02	—	0.07 ± 0.03	—
O(3P_1)	—	0.03 ± 0.02	—	0.05 ± 0.02

expected for the measured $\text{Im}[A_1^{(1)}]$ parameters and this will be considered in the next section.

5.8.3 Rotational depolarisation of measured polarisation parameters

The derivation of equation (5.28) used to simulate the $\text{Im}[A_1^{(1)}]$ parameters assumes the fast dissociation limit, whereby there is no rotation of the parent molecule in the time period between initial photon absorption and dissociation. As discussed in section 5.5, the translational anisotropy parameters, β_2 and β_4 , measured at the same two-photon dissociation wavelengths are reduced from the expected values of 5/7 and $-12/7$ respectively for a $\Sigma \rightarrow \Pi$ excitation in the fast dissociation limit and that this reduction was due to rotation of the parent molecule prior to dissociation. This rotational depolarisation of the photofragment angular distribution due to the long lifetimes of the C ($v = 0$) and ($v = 1$) states will also affect the measured $\text{Im}[A_1^{(1)}]$ parameters.

Rotational depolarisation of measured polarisation parameters has been investigated previously^{43,44} and this will now be extended for a two-photon dissociation. In this work, the treatment of Bougas *et al.*,⁴⁴ which considers the polar angle between ϵ_{phot} and $\mathbf{v}$ at the moment of dissociation, will be used. This angle, θ'_ϵ , is assumed to be related to the angle between ϵ_{phot} and $\mathbf{v}$ at the point of initial photon absorption, θ_ϵ , by the spherical harmonic addition theorem,⁴⁴

$$\cos \theta'_\epsilon = \cos \theta_\epsilon \cos \gamma + \sin \theta_\epsilon \sin \gamma \cos \xi, \quad (5.29)$$

where γ is the classical angle between the molecular axis at the moment of initial photon absorption and dissociation and ξ is the azimuthal angle which includes all possible geometries which yield photofragments recoiling parallel to $\mathbf{v}$. The rotational depolarisation of the measured $\text{Im}[A_1^1]$ parameters is therefore given by

evaluating the integral,

$$\frac{1}{2\pi} \int_0^{2\pi} \cos^3 \theta'_\epsilon \sin \theta'_\epsilon \sin \phi' d\xi, \quad (5.30)$$

which can be equated by substituting in equation (5.29) and evaluating $\sin \phi'$ using equations (6 – 8) of Ref. 44. Thus, equation (5.28) becomes,

$$\begin{aligned} I_{45\text{circ}} = & I_{\text{tot},A}(\text{incoherent}) \\ & + s_1(j) \text{Im}[A_1^{(1)}] \left(\frac{45}{14} d_2 P_0^2(x) + \frac{15}{28} d_4 P_0^4(x) \right), \end{aligned} \quad (5.31)$$

where,

$$d_2 = \frac{1}{2} (2 \cos^2 \gamma + \cos \gamma - 1), \quad (5.32)$$

$$d_4 = \frac{1}{8} (28 \cos^4 \gamma + 7 \cos^3 \gamma - 27 \cos^2 \gamma - 3 \cos \gamma + 3). \quad (5.33)$$

The d_2 depolarisation parameter calculated here is the same as the as the rotational depolarisation calculated in Refs. 43 and 44 for $\text{Im}[a_1^{(1)}]$ parameters following a one-photon dissociation. The higher order d_4 depolarisation parameter is due to the dissociation now being a two-photon process.

As with the translational anisotropy parameters, the quasi-classical approach from Ref. 37 will be used to determine the extent of this depolarisation, by assuming an exponentially decaying distribution of the post excitation angle, γ . The d_k depolarisation factors appearing in equation (5.31) will consequently be replaced by the average parameters, $\langle d_k \rangle$, which when normalised so that $\langle P_0^0(\cos \gamma) \rangle = 1$, are given by,

$$\langle d_2 \rangle = \frac{1}{2} \left(\frac{2 + 5y^2}{1 + 5y^2 + 4y^4} \right), \quad (5.34)$$

$$\langle d_4 \rangle = \frac{1}{4} \left(\frac{4 + 82y^2 + 476y^4 + 803y^6}{1 + 30y^2 + 273y^4 + 820y^6 + 576y^8} \right), \quad (5.35)$$

where y is as defined in equations (5.9) and (5.10). The depolarisation factors $\langle d_2 \rangle$ and $\langle d_4 \rangle$ are calculated for each dissociation wavelength using the values for the lifetime broadening parameter, Γ , experimentally determined in section 5.2 together

with the average J values used in section 5.5 to successfully explain the deviations of the measured translational anisotropy from $\beta_2 = 5/7$ and $\beta_4 = -12/7$. For example, for two-photon dissociation at 305.07 nm y is found to be 0.57, corresponding to $\langle d_2 \rangle = 0.58$ and $\langle d_4 \rangle = 0.37$. The lifetime corrected $\text{Im}[A_1^{(1)}]$ parameters, obtained by fitting the experimental data to equation (5.31), are displayed in table 5.9.

Table 5.9: Lifetime corrected orientation $\text{Im}[A_1^{(1)}]$ parameters for all photofragments determined by fitting experimental difference TOF profiles to equation (5.31).

Fragment	C ($v = 0$)		C ($v = 1$)	
	303.87 nm	305.07 nm	295.44 nm	296.77 nm
O(1D_2)	0.17 ± 0.06	0.14 ± 0.04	0.10 ± 0.03	0.10 ± 0.03
O(3P_2)	0.14 ± 0.06	—	0.07 ± 0.03	—
O(3P_1)	—	0.06 ± 0.03	—	0.05 ± 0.02

5.8.4 Discussion

The coherent orientation observed in this work is attributed to coherent two-photon excitation *via* absorption routes of different symmetry and has the same origin as the coherent orientation parameter, $\text{Im}[a_1^{(1)}(\parallel, \perp)]$, measured in chapter 4 for the photodissociation of Cl₂. As discussed in chapter 4, $\text{Im}[a_1^{(1)}(\parallel, \perp)]$ is proportional to $\sin \Delta\varphi$, whilst the related coherent alignment, $\text{Re}[a_1^{(2)}(\parallel, \perp)]$, is proportional to $\cos \Delta\varphi$, where $\Delta\varphi$ is the asymptotic phase difference between the interfering parallel and perpendicular pathways. This phase difference is found to depend on the dissociation wavelength and consequently the measured $\text{Im}[a_1^{(1)}(\parallel, \perp)]$ and $\text{Re}[a_1^{(2)}(\parallel, \perp)]$ parameters are found to vary (pseudo-)sinusoidally with dissociation wavelength as is seen in figure 4.10. Whilst the dissociation energies used in this work cover a similar energy range to that shown in figure 4.10, the lifetime corrected orientation parameters presented in table 5.9 show very little variation with photolysis wavelength. As mentioned previously, the observed orientation in this case is most likely due to coherent excitation of the $|\Omega| = 1$ spin-orbit components of the C state in

addition to the $|\Omega| = 0$ and 2 components predominantly excited at each of the dissociation wavelengths. The previous alignment measurements have shown the dissociation mechanism to be close to the diabatic limit and the phase difference between the two dissociation pathways is most likely due to the “dynamical phase” resulting from non-adiabatic transitions at large internuclear distances. For Cl₂ photodissociation, where the phase difference arises from adiabatic dissociation along two energetically different pathways, the initially excited part of the potential energy surfaces will clearly have a large effect on the asymptotic phase difference. For the orientation observed in this chapter, however, the phase difference only depends on the long range part of the potential energy surfaces and is therefore expected to be insensitive to the initial excitation energy.

The difference profiles taken in geometry pair G_4 were also fit by including the coherent alignment, $\text{Re}[A_1^{(2)}]$, parameter. It was found that fits were not significantly improved by the inclusion of this parameter and therefore it is concluded that $\text{Re}[A_1^{(2)}]$ must be close to zero for all dissociation wavelengths. The absence of a non-zero $\text{Re}[A_1^{(2)}]$ is most conclusively seen for the O(3P_2) photofragments at 296.77 nm and O(3P_1) photofragments at 295.44 nm where incoherent alignment parameters close to zero were measured, thus ensuring that the coherent alignment is indeed close to zero and its absence is not simply due to the other polarisation parameters masking its contribution to the overall TOF profile. Assuming that this coherent alignment has the same dependence on the asymptotic phase difference between the two dissociation pathways, $\Delta\varphi$, as the $\text{Re}[a_1^2(\parallel, \perp)]$ parameter, the absence of a non-zero $\text{Re}[A_1^{(2)}]$ indicates that the quantity $\cos \Delta\varphi$ is close to zero for the predissociation and, consequently, $\sin \Delta\varphi$ should be close to 1. The measured $\text{Im}[A_1^{(1)}]$ parameters shown in table 5.9 are all small, even when corrected for rotational depolarisation, compared to the physical limiting values for $\text{Im}[a_1^{(1)}]$ of 0.577 and 0.5 for $j = 2$ and 1 respectively.⁷ Since $\sin \Delta\varphi$ should be close to 1, it is therefore expected that $\text{Im}[a_1^{(1)}]$ is close to its maximal value with the small measured orientation being due to the weighting coefficients, c_A and c_B , since $\text{Im}[A_1^{(1)}] = c_A c_B \text{Im}[a_1^{(1)}]$.

As mentioned previously, measured translational anisotropy parameters were found to be consistent with a pure $\Sigma \rightarrow \rightarrow \Pi$ transition at all dissociation wavelengths and therefore any absorption pathway of a different symmetry must be a relatively very small contribution, *i.e.* c_A must be close to 1 and c_B close to zero. This is further confirmed by the spectral simulations of the C $^3\Pi_g$ ($v = 0$) and ($v = 1$) two-photon absorption bands shown in figure 5.2, with the (relative) absorption probability to the $|\Omega| = 1$ component being found to be 5 – 7 % for all dissociation wavelengths. It is therefore concluded that although the two-photon absorption occurs predominantly *via* the $X\ ^3\Sigma_{g,\pm 1}^- \xrightarrow{\mu_{\parallel}} \Sigma_{\pm 1} \xrightarrow{\mu_{\perp}} C\ ^3\Pi_{g,0,\pm 2}$ pathway, absorption *via* pathways of different symmetries, most likely $X\ ^3\Sigma_{g,\pm 1}^- \xrightarrow{\mu_{\parallel}} \Sigma_{\pm 1} \xrightarrow{\mu_{\parallel}} C\ ^3\Pi_{g,\pm 1}$, do contribute to the overall absorption process and are manifest in the atomic photofragment's electronic angular momentum polarisation.

5.9 Conclusions

(2+1) REMPI spectra have been taken of O₂ X $^3\Sigma_g^-$ ionised *via* the C $^3\Pi_g$ ($v = 0$) and ($v = 1$) Rydberg states. These spectra have been fitted to spectral simulations to determine lifetime broadening parameters of $28 \pm 5\text{ cm}^{-1}$ for C ($v = 0$) and $152 \pm 10\text{ cm}^{-1}$ for C ($v = 1$), consistent with previous literature values. Both O($^3P_{j=0,1,2}$) and O(1D_2) photofragments produced as a result of the predissociation of the C $^3\Pi_g$ ($v = 0$) and ($v = 1$) Rydberg states accessed *via* two-photon absorption have subsequently been measured and analysed by extending the polarisation parameter formalism used in chapter 4 to describe atomic angular momentum alignment following two-photon dissociation. O(3P_j) TOF profiles have been used to determine the dissociation limit branching ratio of 0.1 ± 0.05 , which is consistent with previous experimental and theoretical measurements in indicating that the diabatic O(1D_2) + O(3P_j) channel is the major dissociation pathway.

Translational anisotropy parameters have been measured for O($^3P_{j=0,1,2}$) and O(1D_2) photofragments and are all found to be reduced from the limiting values of $\beta_2 = 5/7$ and $\beta_4 = -12/7$ predicted for dissociation following a $\Sigma \rightarrow \rightarrow \Pi$

transition. The reduction is found to be in agreement with the predicted rotational depolarisation of the translational anisotropy due to the long lifetime of the predissociated states. The angular momentum polarisation of both fragments has been measured and the alignment, as well as spin-orbit branching ratios, of the O(3P_j) photofragments are found to be best described by a diabatic model using the measured O(1D_2) alignment.

In addition, the atomic angular momentum has been found to be oriented and this orientation has been interpreted in terms of a coherent, $\text{Im}[A_1^{(1)}]$, orientation polarisation parameter resulting from interference between absorption pathways of different symmetry. This measured orientation is found to be sensitive to the two-photon absorption wavelength, with predissociation from C ($v = 1$) resulting in a larger orientation than from C ($v = 0$). However, once the effect of rotational depolarisation has been accounted for, the orientation is found to be relatively constant for all dissociation wavelengths. The lifetime corrected values of $\text{Im}[A_1^{(1)}]$ are found to be much smaller than their limiting values and indicate that two-photon absorption occurs almost exclusively *via* a single absorption pathway to the $|\Omega| = 0$ or 2 components of the C state, with a small contribution from absorption to the $|\Omega| = 1$ component.

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Chapter 6

General conclusions and future work

This thesis has shown how the REMPI-TOF technique may be used to study the UV photodissociation dynamics of small gas phase molecules. REMPI has been used to state-selectively detect both atomic and molecular photofragments and TOF profiles of these photofragments have been recorded in a number of experimental geometries in order to determine the translational anisotropy and angular momentum polarisation of the fragments.

In chapter 3, the photodissociation of NO_2 at 320 nm is investigated. In order to lower the rotational temperature of the molecular beam, a skimmer was incorporated into the experimental setup and the angular momentum polarisation of the NO photofragments was measured in terms of the semi-classical bipolar moments. The translational anisotropy of the NO ($N = 30$) photofragments is found to be $\beta = 1.38 \pm 0.06$ and, once the role of parent molecular rotations and non-axial recoil have been accounted for, is found to be consistent with dissociation occurring with an NO_2 bond angle of 128° , slightly reduced from the ground state equilibrium bond angle of 134.25° . This measured value of β is slightly larger than previous measurements, which used a rotationally hotter source, and it was found that the deviations between the two measurements were due to parent molecular rotations. The angular momentum alignment was found to be largely consistent with an impulsive model, with $\boldsymbol{\mu}$ and $\mathbf{v}$ in the same molecular plane and both preferentially perpendicular to $\mathbf{J}$, whilst orientation measurements provide evidence for an additional torque due

to the NO₂ bond opening during the dissociation.

In chapter 4, the UV photodissociation of Cl₂ is studied and the angular momentum polarisation of the resulting Cl fragments has been measured in terms of a polarisation parameter formalism. The translational anisotropy of Cl(²P_{3/2}) is found to be within error of the limiting value of $\beta = -1$ and is consistent with the (Cl + Cl) dissociation channel occurring following a pure perpendicular excitation to the C ¹Π_{1u} state. The alignment of the Cl atoms has been measured and is found to deviate from the values of $a_0^{(2)}(\perp) = -0.8$ and $a_2^{(2)}(\perp) = 0$ predicted for adiabatic dissociation along the C state (for example, $a_0^{(2)}(\perp) = -0.68 \pm 0.13$ and $a_2^{(2)}(\perp) = -0.34 \pm 0.1$ for dissociation at 320 nm). These deviations are due to non-adiabatic transitions to the A ³Π_{1u} state. The extent of these non-adiabatic transitions has been determined from the measured polarisation parameters and found to be consistent with theoretical predictions. The translational anisotropy of Cl*(²P_{1/2}) is found to vary with dissociation wavelength and is found to change from being predominantly perpendicular at 320 nm ($\beta = -0.30 \pm 0.07$) to parallel at 330 nm ($\beta = 0.32 \pm 0.07$). This is consistent with the (Cl + Cl*) dissociation channel resulting from coherent excitation to both the B ³Π_{0+u} and C ¹Π_{1u} states and the interference between these two possible dissociation pathways is found to result in angular momentum orientation. This orientation depends on the phase difference between the two dissociation pathways and is consequently found to depend on both the dissociation wavelength and the isotopic mass of the Cl* atom probed.

In chapter 5, the predissociation dynamics of the C ³Π_g ($v = 0$) and ($v = 1$) Rydberg states has been studied. (2+1) REMPI spectra have been taken of O₂ X ³Σ_g⁻ excited *via* both these states and the spectra have been fitted to spectral simulations in order to determine lifetime broadening parameters of 28 ± 5 cm⁻¹ for C ($v = 0$) and 152 ± 10 cm⁻¹ for C ($v = 1$), consistent with previous literature values. TOF profiles of both O(³P_{*j*=0,1,2}) and O(¹D₂) photofragments produced as a result of the predissociation of the C ($v = 0$) and ($v = 1$) Rydberg states have been recorded in multiple geometries and the angular momentum polarisation of

these fragments has been interpreted in terms of a polarisation parameter formalism, which has been extended for two-photon dissociation. $O(^3P_j)$ TOF profiles have been used to determine the dissociation limit branching ratio of 0.1 ± 0.05 , which is consistent with previous experimental and theoretical measurements in indicating that the diabatic $O(^1D_2) + O(^3P_j)$ channel is the major dissociation pathway. Translational anisotropy parameters have been measured for these photofragments and are all found to be reduced from the limiting values of $\beta_2 = 5/7$ and $\beta_4 = -12/7$ predicted for dissociation following a $\Sigma \rightarrow \Pi$ transition, with the reduction found to be in agreement with the predicted rotational depolarisation of the translational anisotropy due to the long lifetime of the predissociated states. The angular momentum alignment of both co-fragments has been measured and the relationship between the $O(^1D_2)$ and $O(^3P_j)$ alignment is found to be consistent with the dissociation occurring diabatically.

In addition to being aligned, both co-fragments were found to have oriented angular momentum. This observed orientation must be caused by interference between coherently excited pathways of different symmetries. The origin of this orientation has been considered and it is concluded that the most likely cause of this orientation is coherent excitation of different spin-orbit components of the C state. A further possible experiment, which may help to confirm the origin of this orientation, would be to probe the $d\ ^1\Pi_g$ Rydberg state, which is accessed at similar two-photon wavelengths and is also predissociated. This state will have only one spin-orbit component and, therefore, if coherent orientation is also observed following predissociation from this state then an alternative explanation for the origin of the orientation, possibly coupling between the C and d states, must be found.

Appendix A

TOF profile shape in terms of bipolar moments

The shape of the TOF profile for one-photon dissociation and $(1 + 1')$ REMPI probing, as used to probe NO photofragments in chapter 3, may be written in the form,

$$I = g_0 + g_2 P_2(x) + g_4 P_4(x), \quad (\text{A.1})$$

where $P_k(x)$ are Legendre polynomials of order k in terms of the TOF shift x . The expansion coefficients, g_k , will depend on the line-strength factors, $h^{(k)}(J)$, which are given in table 3.1, the bipolar moments, $\beta_Q^K(k_1 k_2)$, defined in section 3.2.1 and the angles θ_D and χ_p illustrated in figure 3.1 which define the geometry of the photolysis and probe laser beams respectively. For linear polarised, counter-propagating photolysis and probe laser beams these coefficients are given by,

$$g_0 = 1 + \frac{4}{5} h^{(2)}(J) \beta_0^2(0, 2) P_2(\cos \chi_p), \quad (\text{A.2})$$

$$\begin{aligned}
g_2 = & 2 \beta_0^2(2, 0) P_2(\cos \theta_D) \\
& + 2 h^{(2)}(J) \beta_0^0(2, 2) \begin{pmatrix} P_2(\cos \theta_D) P_2(\cos \chi_p) \\ +3 \sin \theta_D \cos \theta_D \sin \chi_p \cos \chi_p \\ +\frac{3}{4} \sin^2 \theta_D \sin^2 \chi_p \end{pmatrix} \\
& - \frac{2}{7} h^{(2)}(J) \beta_0^2(2, 2) \begin{pmatrix} 4 P_2(\cos \theta_D) P_2(\cos \chi_p) \\ +6 \sin \theta_D \cos \theta_D \sin \chi_p \cos \chi_p \\ -3 \sin^2 \theta_D \sin^2 \chi_p \end{pmatrix}, \tag{A.3}
\end{aligned}$$

$$g_4 = \frac{6}{7} h^{(2)}(J) \beta_0^2(4, 2) \begin{pmatrix} \frac{12}{5} P_4(\cos \theta_D) P_2(\cos \chi_p) \\ +3 \sin \theta_D \cos \theta_D (7 \cos^2 \theta_D - 3) \sin \chi_p \cos \chi_p \\ +\frac{3}{4} \sin^2 \theta_D (7 \cos^2 \theta_D - 1) \sin^2 \chi_p \end{pmatrix}. \tag{A.4}$$

Appendix B

TOF profile shape following two-photon dissociation

The expressions for the measured TOF profiles have been calculated using the method described in the text and are given in the form,

$$I = g_0 + g_2P_2(x) + g_4P_4(x) + g_6P_6(x) + g_8P_8(x), \quad (\text{B.1})$$

where $P_k(x)$ are Legendre polynomials of order k in terms of the TOF shift x . g_k are coefficients which will depend on the probe transition sensitivity factors, s_k , the translational anisotropy parameters, β_2 and β_4 , and the polarisation parameters, a_q^k . These will be unique for each experimental geometry defined by the laboratory frame angles θ_D , Θ and Φ defined in section 5.3. For linear polarised photolysis and probe light, the angles θ_D and Θ describe the angle between the electric vector of the laser beam and the TOF axis for the photolysis and probe laser beams respectively, whilst $\Phi = 0$ for the counter-propagating laser beams used in this thesis. Expressions for each TOF profile, I_{dma} , I_{Hma} , I_{Vma} and I_{maH} , required for geometries G_1 , G_3 and G_4 , used to determine the translational anisotropy and angular momentum alignment

of the oxygen atoms in chapter 5, have been calculated to be,

$$\begin{aligned}
I_{dma} = & \left[1 + \frac{1}{5}s_2\beta_2a_0^{(2)} + \frac{2}{7}\sqrt{6}s_2a_2^{(2)} + s_4 \left(\frac{1}{9}\beta_4a_0^{(4)} + \frac{4}{21}\sqrt{10}a_2^{(4)} \right) \right] \\
& + \left[-\frac{7}{18}\beta_4 + s_2 \left(\left(-\frac{1}{5}\beta_2 - \frac{10}{99}\beta_4 \right) a_0^{(2)} + \frac{7}{11}\sqrt{\frac{2}{3}}a_2^{(2)} \right) \right. \\
& + s_4 \left(\left(-\frac{7}{18} - \frac{10}{99}\beta_2 - \frac{9}{143}\beta_4 \right) a_0^{(4)} + \frac{28}{143}\sqrt{10}a_2^{(4)} \right) \left. \right] P_4(x) \\
& + \left[s_2 \left(\frac{10}{99}\beta_4a_0^{(2)} + \frac{40}{231}\sqrt{\frac{2}{3}}a_2^{(2)} \right) \right. \\
& + s_4 \left(\left(\frac{10}{99}\beta_2 + \frac{40}{891}\beta_4 \right) a_0^{(4)} - \frac{116}{2079}\sqrt{10}a_2^{(4)} \right) \left. \right] P_6(x) \\
& + \left[s_4 \left(\frac{245}{4212}\beta_4a_0^{(4)} + \frac{14}{351}\sqrt{10}a_2^{(4)} \right) \right] P_8(x),
\end{aligned} \tag{B.2}$$

$$\begin{aligned}
I_{Hma} = & \left[1 - s_4 \left(\frac{7}{162}\beta_4a_0^{(4)} + \frac{2}{27}\sqrt{10}a_2^{(4)} \right) \right] \\
& + \left[\beta_2 + s_4 \left(\left(-\frac{1}{9}\beta_2 - \frac{50}{891}\beta_4 \right) a_0^{(4)} - \frac{35}{297}\sqrt{10}a_2^{(4)} \right) \right] P_2(x) \\
& + \left[\beta_4 + s_4 \left(\left(-\frac{7}{18} - \frac{10}{99}\beta_2 - \frac{9}{143}\beta_4 \right) a_0^{(4)} + \frac{28}{143}\sqrt{10}a_2^{(4)} \right) \right] P_4(x) \\
& + \left[s_4 \left(\left(-\frac{35}{198}\beta_2 - \frac{70}{891}\beta_4 \right) a_0^{(4)} + \frac{29}{297}\sqrt{10}a_2^{(4)} \right) \right] P_6(x) \\
& - \left[s_4 \left(\frac{1715}{11583}\beta_4a_0^{(4)} + \frac{392}{3861}\sqrt{10}a_2^{(4)} \right) \right] P_8(x),
\end{aligned} \tag{B.3}$$

$$\begin{aligned}
I_{Vma} = & \left[1 + s_2 \left(\frac{1}{10} \beta_2 a_0^{(2)} + \frac{1}{7} \sqrt{6} a_2^{(2)} \right) - s_4 \left(\frac{13}{648} \beta_4 a_0^{(4)} + \frac{13}{189} \sqrt{\frac{5}{2}} a_2^{(4)} \right) \right] \\
& + \left[s_2 \left(-\frac{1}{2} \beta_2 + \frac{5}{7\sqrt{6}} a_2^{(2)} \right) \right. \\
& + s_4 \left(\left(\frac{17}{126} \beta_2 - \frac{1075}{12474} \beta_4 \right) a_0^{(4)} + \frac{155}{2079} \sqrt{\frac{5}{2}} a_2^{(4)} \right) \left. \right] P_2(x) \\
& + \left[\frac{3}{8} \beta_4 + s_2 \left(\frac{15}{154} \beta_2 a_0^{(2)} - \frac{37}{77} \sqrt{\frac{3}{2}} a_2^{(2)} \right) \right. \\
& + s_4 \left(\left(-\frac{7}{18} - \frac{5}{63} \beta_2 + \frac{69}{2002} \beta_4 \right) a_0^{(4)} + \frac{6}{91} \sqrt{10} a_2^{(4)} \right) \left. \right] P_4(x) \\
& + \left[s_2 \left(\frac{5}{132} \beta_4 a_0^{(2)} - \frac{5}{77} \sqrt{\frac{2}{3}} a_2^{(2)} \right) \right. \\
& + s_4 \left(\left(\frac{5}{36} \beta_2 + \frac{20}{891} \beta_4 \right) a_0^{(4)} - \frac{1}{189} \sqrt{\frac{5}{2}} a_2^{(4)} \right) \left. \right] P_6(x) \\
& - s_4 \left[\frac{511}{3861} \sqrt{\frac{5}{2}} a_2^{(4)} + \frac{17885}{185328} \beta_4 a_0^{(4)} \right] P_8(x),
\end{aligned} \tag{B.4}$$

$$\begin{aligned}
I_{maH} = & \left[1 - s_4 \left(\frac{2}{27} \sqrt{10} a_2^{(4)} + \frac{7}{162} \beta_4 a_0^{(4)} \right) \right] \\
& + \left[s_2 \left(\left(1 - \frac{1}{9} \beta_4 \right) a_0^{(2)} - \frac{10}{21} \sqrt{\frac{2}{3}} a_2^{(2)} \right) \right. \\
& - s_4 \left(\frac{50}{891} \beta_4 a_0^{(4)} + \frac{80}{2079} \sqrt{10} a_2^{(4)} \right) \left. \right] P_2(x) \\
& + \left[-\frac{7}{18} \beta_4 + s_2 \left(-\frac{10}{99} \beta_4 a_0^{(2)} + \frac{20}{77} \sqrt{6} a_2^{(2)} \right) \right. \\
& + s_4 \left(\left(1 - \frac{9}{143} \beta_4 \right) a_0^{(4)} + \frac{6}{91} \sqrt{10} a_2^{(4)} \right) \left. \right] P_4(x) \\
& + \left[-s_2 \left(\frac{35}{198} \beta_4 a_0^{(2)} + \frac{10}{33} \sqrt{\frac{2}{3}} a_2^{(2)} \right) \right. \\
& + s_4 \left(-\frac{70}{891} \beta_4 a_0^{(4)} + \frac{4}{27} \sqrt{10} a_2^{(4)} \right) \left. \right] P_6(x) \\
& - \left[s_4 \left(\frac{1715}{11583} \beta_4 a_0^{(4)} + \frac{392}{3861} \sqrt{10} a_2^{(4)} \right) \right] P_8(x),
\end{aligned} \tag{B.5}$$

$$\begin{aligned}
I_{maV} = & \left[1 + s_2 \left(\frac{1}{10} \beta_2 a_0^{(2)} + \frac{1}{7} \sqrt{6} a_2^{(2)} \right) - s_4 \left(\frac{13}{648} \beta_4 a_0^{(4)} + \frac{13}{189} \sqrt{\frac{5}{2}} a_2^{(4)} \right) \right] \\
& + \left[s_2 \left(\left(-\frac{1}{2} - \frac{1}{7} \beta_2 + \frac{17}{126} \beta_4 \right) a_0^{(2)} + \frac{25}{21} \sqrt{\frac{2}{3}} a_2^{(2)} \right) \right. \\
& + s_4 \left(a_0^{(4)} \left(-\frac{5}{84} \beta_2 - \frac{1075}{12474} \beta_4 \right) - \frac{845}{4158} \sqrt{\frac{5}{2}} a_2^{(4)} \right) \left. \right] P_2(x) \\
& + \left[-\frac{7}{18} \beta_4 + s_2 \left(\left(\frac{3}{70} \beta_2 - \frac{5}{63} \beta_4 \right) a_0^{(2)} + \frac{3}{7} \sqrt{\frac{3}{2}} a_2^{(2)} \right) \right. \\
& + s_4 \left(\left(\frac{3}{8} + \frac{15}{154} \beta_2 + \frac{69}{2002} \beta_4 \right) a_0^{(4)} - \frac{323}{1001} \sqrt{\frac{5}{2}} a_2^{(4)} \right) \left. \right] P_4(x) \\
& + \left[s_2 \left(\frac{5}{36} \beta_4 a_0^{(2)} + \frac{5}{21} \sqrt{\frac{2}{3}} a_2^{(2)} \right) \right. \\
& + s_4 \left(\left(-\frac{5}{132} \beta_2 + \frac{20}{891} \beta_4 \right) a_0^{(4)} - \frac{221}{2079} \sqrt{\frac{5}{2}} a_2^{(4)} \right) \left. \right] P_6(x) \\
& - \left[s_4 \left(\frac{17885}{185328} \beta_4 a_0^{(4)} + \frac{511}{3861} \sqrt{\frac{5}{2}} a_2^{(4)} \right) \right] P_8(x).
\end{aligned} \tag{B.6}$$

For linear photolysis and circularly polarised probe light, the angle θ_D is still the angle between the electric vector of the linear polarised photolysis laser beam and Θ and Φ are now both 90° . For profiles taken in geometry G_5 , the TOF profile shape

is calculated to be,

$$\begin{aligned}
I_{45\text{circ}} = & \left[1 - s_2 \left(\frac{1}{10} \beta_2 a_0^{(2)} + \frac{1}{7} \sqrt{6} a_2^{(2)} \right) + s_4 \left(\frac{1}{24} \beta_4 a_0^{(4)} + \frac{1}{7} \sqrt{\frac{5}{2}} a_2^{(4)} \right) \right] \\
& + \left[\frac{1}{4} \beta_2 + \frac{45}{14} s_1 \text{Im}[A_1^{(1)}] + s_2 \left(\left(-\frac{27}{280} \beta_2 + \frac{145}{616} \beta_4 \right) a_0^{(2)} - \frac{387}{308} \sqrt{\frac{3}{2}} a_2^{(2)} \right) \right. \\
& + s_4 \left(a_0^{(4)} \left(\frac{3}{8} - \frac{15}{308} \beta_2 - \frac{369}{8008} \beta_4 \right) + \frac{111}{1001} \sqrt{10} a_2^{(4)} \right) \left. \right] P_2(x) \\
& + \left[-\frac{13}{32} \beta_4 + \frac{15}{28} s_1 \text{Im}[A_1^{(1)}] + s_2 \left(\left(-\frac{27}{280} \beta_2 + \frac{145}{616} \beta_4 \right) a_0^{(2)} + \frac{387}{308} \sqrt{\frac{3}{2}} a_2^{(2)} \right) \right. \\
& + s_4 \left(\left(\frac{3}{8} - \frac{15}{308} \beta_2 - \frac{369}{8008} \beta_4 \right) a_0^{(4)} + \frac{111}{1001} \sqrt{10} a_2^{(4)} \right) \left. \right] P_4(x) \\
& + \left[s_2 \left(\frac{15}{704} \beta_4 a_0^{(2)} + \frac{15}{616} \sqrt{\frac{3}{2}} a_2^{(2)} \right) \right. \\
& + s_4 \left(\left(\frac{25}{352} \beta_2 - \frac{65}{528} \beta_4 \right) a_0^{(4)} + \frac{311}{616} \sqrt{\frac{5}{2}} a_2^{(4)} \right) \left. \right] P_6(x) \\
& + \left[s_4 \left(\frac{245}{109824} \beta_4 a_0^{(4)} + \frac{7}{2288} \sqrt{\frac{5}{2}} a_2^{(4)} \right) \right] P_8(x).
\end{aligned}
\tag{B.7}$$

List of Publications

“Electronic polarization effects in the photodissociation of Cl₂.”

E. K. Campbell, A. B. Alekseyev, G. G. Balint-Kurti, M. Brouard, A. Brown, R. J. Buenker, R. Cireasa, A. J. Gilchrist, A. J. Johnsen, D. B. Kokh, S. Lucas, G. A. D. Ritchie, T. R. Sharples and B. Winter

J. Chem. Phys. **136**, 164311 (2012).

“Predissociation dynamics of the C ³Π_g Rydberg state of molecular oxygen.”

A. J. Gilchrist and G. A. D. Ritchie

J. Chem. Phys. **138**, 104320 (2013).

“Atomic orientation following predissociation of the C ³Π_g Rydberg state of molecular oxygen.”

A. J. Gilchrist and G. A. D. Ritchie

J. Chem. Phys. **138**, 214307 (2013).