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INVITED ARTICLE

Angular momentum polarisation in the O(1D) products of O₂ photolysis via the B³Σ⁻ u state

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The first fully allowed spectroscopic transition in O₂ is the B³Σ⁻ u ← X³Σ⁺ g transition comprising the well-known Schumann–Runge bands and continuum. We report a velocity-map imaging study in which the O(1D) angular momentum polarisation and O(3P) spin–orbit branching ratios arising from this process have been measured. We show that direct 157 nm excitation into the Schumann–Runge continuum leads to extremely strong angular momentum polarisation in the O(1D) product. Comparison with previous studies indicates that this is a general feature of dissociation via the B state. The fine structure branching ratios in the co-fragment O(3P J = 2, 1, 0) were measured to be 88.5:1.6:9.7:1.4:1.9. Based on a consideration of the Massey parameter for the system, the data were modelled using theoretical calculations based on adiabatic and diabatic models of the dissociation. While both models were able to describe some aspects of the dissociation accurately, neither was able to predict both the fine structure branching ratios of the O(3P) products and the O(1D2) alignment. We have also investigated O(1D2) alignment arising from 203.8 and 205.5 nm photodissociation via the B³Σ⁻ u state of O₂ vibrationally excited to v=6–11. As in the 157 nm photodissociation of vibrationally ground state O₂, strong polarisation of the O(1D2) photofragments is observed.

Keywords: photodissociation; molecular oxygen; O(1D); polarisation; Schumann–Runge

1. Introduction

The atmospheric importance of the O₂ molecule has led to considerable interest in studying its photochemistry; in particular, the UV photodissociation of molecular oxygen following absorption below 200 nm marks the first step in atmospheric oxygen photochemistry, and has been a particular target for investigations [1,2].

The photochemistry and spectroscopy of O₂ is far from straightforward, due to the strong optical selection rules and complex multiplet structure arising from the open-shell (1σg²1σu²2σg²2σu²1πg²3σg²1πu²) electronic structure of the ground state. However, the development of increasingly sophisticated imaging techniques for studying molecular photodissociation processes, and the resulting ability to characterise the products, is providing ever deeper insights into the complex photochemistry of the O₂ molecule. Of particular relevance to this study, the ability to quantify angular momentum polarisation in the photofragments, and therefore to determine the populations of the M_J or M_L sublevels, provides detailed insights into the evolution of the system over the various available potential energy surfaces during the dissociation.

The UV spectroscopy of O₂ has been well characterised, and is summarised in Figure 1. The first observed bands, known as the Herzberg bands, occur between 242 and 270 nm. These are low intensity signals corresponding to formally forbidden transitions from the electronic ground state to the A³Σ⁺ g, A³Δ u and c¹Σ⁻ g states. At shorter wavelengths between 180 and 242 nm, above the dissociation threshold for these states, photofragmentation to the O(3P) + O(3P) atomic states gives rise to the Herzberg continuum.

The first fully allowed spectroscopic transition from the ground state of O₂ is to the B³Σ⁻ u state, giving rise to the strong Schumann–Runge bands. This transition in O₂ within the Earth’s atmosphere at
altitudes of 80–100 km is responsible for blocking VUV light in the solar spectrum from reaching the Earth’s surface, and is also the origin of the definition of the vacuum ultraviolet region of the spectrum. The transition dominates the O₂ absorption spectrum, and is the focus of this paper. At wavelengths shorter than 175 nm, dissociation of the B state occurs via the process

\[ O₂ + hν \rightarrow O(^1D) + O(^3P) + E', \]  

where \( E' \) is the translational energy of the fragments. The bond dissociation energy, \( D_0 \), of O₂ is 5.117 eV, and the metastable \( O(^1D) \) photofragment has an electronic energy of 1.967 eV. This marks the onset of the Schumann–Runge continuum. Further resolved band structure at wavelengths below 130 nm corresponds to excitation of Rydberg-valence complexes.

We report the results of a recent study of O₂ dissociation at a wavelength of 157 nm, which corresponds to direct excitation into the Schumann–Runge continuum above the dissociation threshold for the B state. Photodissociation at this wavelength has been studied previously both experimentally and theoretically. The absorption cross-section at 157 nm is \( 8 \times 10^{-18} \) cm², and the various accessible dissociation pathways and their branching ratios [5] are summarised below.

\[
\begin{align*}
&\text{O}_2(X^3\Sigma^-_u, v = 0) + h\nu(157\text{nm}) \\
&\rightarrow k_1 \rightarrow O(^1D_2) + O(^3P_J) + \phi = 0.9945 \\
&\rightarrow k_2 \rightarrow O(^3P_J) + O(^3P_J) + \phi = 0.0055
\end{align*}
\]

The quantum yield for the \( O(^1D) + O(^3P) \) channel is known to be close to unity [6] over a wide range of photolysis wavelengths from 139–175 nm. The relative values of the various rate constants appearing in the reaction scheme above may be inferred from the measured spatial anisotropy parameters \( \beta \) for the two pathways. The pathway leading to \( O(^1D) + O(^3P) \) products occurs via direct dissociation following a \( \Sigma \rightarrow \Sigma \) transition, and unsurprisingly, its \( \beta \) parameter has been measured [5] to be \( 1.98 \pm 0.04 \). For the second product channel, producing \( O(^3P) + O(^3P) \) products, the \( \beta \) parameter is found to be \( 0.92 \pm 0.02 \). Analysis of this result implies a ratio \( k_1 : k_2 = 1 : 0.0019 \) and \( k_1 : k_{12} = 1 : 0.0036 \). These results are in good agreement with theoretical work by Balakrishnan et al. [7], which included predictions of the partial absorption cross-sections for the \( B \leftrightarrow X \) and \( a \leftrightarrow X \) transitions and also the spin–orbit interactions between the \( B \) state and a number of other states converging to the \( O(^3P) + O(^3P) \) atomic limit.

One of the key results of the present study is a determination of the polarisation of electronic angular momentum in the \( O(^1D) \) products of O₂ photolysis at 157 nm. These measurements allow us to determine the populations of the \( M_J \) sublevels (quantised along the photofragment recoil direction) and also to obtain the unpaired electron density distribution in the nascent fragments. The photofragment \( M_J \) populations provide a sensitive probe of the potential energy surfaces involved in the exit channel of the dissociation and the interactions between them. In particular, we will show, through comparison of our data with theoretical models, that the speed at which the dissociation proceeds...
can have a profound effect on the product angular momentum alignment.

We also report the spin–orbit branching ratios in the \(^3\text{P}_J\) coproducts, which provide further insight into the dissociation dynamics. We compare our results with previous alignment measurements by Eppink \textit{et al.} \cite{4} and spin–orbit branching measurements by Huang and Gordon \cite{8} and Matsumi and Kawasaki \cite{9,10}.

A summary of previous experiments yielding information on O\(^{1\text{D}}_2\) alignment is shown in Figure 2.

2. Methods

2.1. Experimental

The velocity-map imaging apparatus has been described previously \cite{11}. The apparatus consists of a source chamber and detection chamber separated by a 2 mm skimmer. For the \(\text{O}_2\) experiments, neat \(\text{O}_2\) gas at a stagnation pressure of 1.5 atm is expanded from a pulsed valve. In some of the experiments a discharge source was used to create vibrationally excited \(\text{O}_2\) in order to access a broader energy range within the Schumann–Runge continuum. The discharge was produced using a static 2 kV potential on a discharge ring positioned in front of the pulsed valve orifice. In both cases, the collimated beam passing through the skimmer is incident on a standard velocity-map imaging ion optics assembly.

For the experiments on ground-state \(\text{O}_2\) the molecular beam is intercepted by a pulse of 157 nm photolysis light from a small F\(_2\) excimer laser (Neweks PSX-100, 0.3 mJ, 5 ns per pulse), and after a time delay of a few nanoseconds the atomic \(\text{O}^{1\text{D}}\) and \(\text{O}^{3\text{P}}\) products are ionised through a \(2+1\)REMPI scheme (see details in description of experimental geometries below) by a second pulse from a Nd:YAG-pumped dye laser (Continuum Surelite III-10 pumping a Radiant Dyes NarrowScan Jaguar dye laser). In the case of the vibrationally excited \(\text{O}_2\) parent, both the photolysis and probe radiation was provided by the dye laser.

Both laser beams are focused onto the molecular beam in order to provide sufficient light intensity in the interaction region. The electrostatic field maintained between the ion lenses is tuned such that the ionised photofragments are accelerated along the flight tube and imaged onto a position sensitive detector consisting of a pair of chevron microchannel plates coupled to a phosphor screen (Burle). By adjusting the ion lens potentials and the gating pulse applied to the microchannel plates, images may be acquired in either ‘crushed’ mode, in which the entire 3D product velocity distribution is projected onto the 2D detector, or ‘sliced’ mode, in which only a thin centre slice of the full 3D distribution is imaged. The velocity-map images appearing on the phosphor screen are captured by a CCD camera and summed on a PC for later processing and analysis. For the crushed images, the repeller potential was set to 1500 V and the effective width of the detector time gate was 100 ns. For slice imaging, the repeller potential was 600 V and the gate was 14 ns, yielding a degree of slicing of around 14%. Background images produced under pump-only and probe-only conditions were subtracted from each pump–probe image.

The multiplet \((J)\) state distribution in the \(\text{O}^{3\text{P}}_J\) atomic product was recorded using two different \(2+1\)REMPI schemes, via the \(3\text{p}^2\text{P}\) and \(4\text{p}^2\text{P}\) states, respectively. The resonance (vacuum) wavelengths for the REMPI schemes used for \(\text{O}^{3\text{P}}_J\) in \(J=0, 1,\) and 2 are 226.23, 226.06, 225.65 nm via the \(3\text{p}^2\text{P}\) state, and 201.10, 200.96, and 200.64 nm via the \(4\text{p}^2\text{P}\) state. Images were recorded with both the pump/photolysis and probe laser polarised in the image plane.

In order to probe angular momentum polarisation in the \(\text{O}^{1\text{D}}_2\) photofragments arising from 157 nm photolysis of vibrationally ground state \(\text{O}_2\), images were acquired in a number of different experimental geometries, defined by the propagation and polarisation directions of the photolysis and probe laser beams and the \(2+1\)REMPI scheme chosen to probe the atomic photofragments. Two \(2+1\)REMPI schemes were employed, in which \(\text{O}^{1\text{D}}\) was ionised either via
the $3p^1F_1$ state at a wavelength of 203.815 nm, or via the $3p^1P_1$ state at 205.473 nm. For each of these transitions, four combinations of laser polarisation and propagation directions were employed, as listed below. The angles accompanying the description of each geometry will be explained in the following section.

1. HHc: pump and probe lasers counterpropagating and both polarised in the image plane ($\Gamma = \pi/2$, $\Delta = 0$, $\Phi = 0$).
2. HVc: pump and probe lasers counterpropagating and polarised parallel and perpendicular to the image plane, respectively ($\Gamma = \pi/2$, $\Delta = 0$, $\Phi = 0$).
3. HHo: as for HHc but with pump and probe propagating orthogonally.
4. HVo: as for HVc but with pump and probe propagating orthogonally.

Images were recorded in both sliced and crushed mode for each geometry.

As noted above, in the case of vibrationally excited O$_2$ molecules, the internal energy is sufficient that photodissociation via the $B$ state and (2+1)REMPI detection is possible using only photons from the probe laser. The images shown in Figure 6 (see Section 3.3) were recorded with the laser polarised in the image plane, a geometry equivalent to the HHc geometry above.

In all cases, the laser power was carefully maintained in order to avoid saturation effects. To correct for the Doppler effect due to fast product recoil and narrow laser bandwidth, the probe laser wavelength was scanned over the transition to ensure that all photofragments were detected and imaged, regardless of their velocity.

2.2. Data analysis

Appendix 1 describes the procedures followed to derive analytical expressions for images recorded in the various experimental geometries. These are based on the formalism developed to describe atomic alignment by Rakitzis and Zare [12]. As described in the appendix, the intensity distribution over the image is a function of a set of alignment parameters (with only $d^{(2)}_0(\parallel)$ and $d^{(4)}_0(\parallel)$ non-zero for a pure parallel transition of the type considered here) and the REMPI sensitivity parameters $s_2$ and $s_4$. These latter parameters depend on the $J$ values of the initial, intermediate, and final states in the REMPI transition used to ionise the photofragments [13–15].

The alignment parameters $d^{(k)}_q(\cdot)$ are determined by fitting these equations to the experimental data. The image equations take the form of a Fourier cosine series, with only even terms non-zero.

$$I(r, \phi) = c_0(r) + c_2(r)\cos 2\phi + c_4(r)\cos 4\phi + c_6(r)\cos 6\phi.$$ 

(4)

To speed up computation, we can therefore reduce the 2D fit to a series of 1D fits by fitting Fourier moments of the image. For O$^{(1)D_2}$ detected via (2+1)REMPI, only terms in the sum up to $n = 6$ need be retained. The Fourier coefficients $c_n(r)$, which are functions of the radial coordinate $r$ of the image (i.e. the projection of the photofragment velocity onto the image plane), may be extracted directly from the experimental images $I(r, \phi)$ by carrying out the appropriate integrals over the angular coordinate $\phi$.

$$c_n(r) = N \int_0^{2\pi} I(r, \phi) \cos (n\phi)r_dr_d\phi,$$

(5)

where the normalisation constant $N$ is equal to 1 when $n = 0$ and 2 when $n > 0$. For the geometries employed, it is straightforward to identify the Fourier coefficients from the analytical expressions for the images by matching terms with Equation (4). By carrying out a simultaneous fit of these analytical expressions for the Fourier coefficients to the corresponding experimentally measured quantities $c_n(r)$, with the $d^{(k)}_q(\cdot)$ as fitting parameters, the alignment parameters may be determined.

3. Results

3.1. Multiplet state distributions of O$^{(3)P_{J=0,1,2}}$

As noted in Section 2.1, we have used velocity-map imaging, employing two different (2+1)REMPI detection schemes, to determine the relative multiplet state populations of the O$^{(3)P_J}$ products. Previously, Huang and Gordon [8] and Matsumi and Kawasaki [9] have carried out laser pump–probe experiments with LIF and (2+1)REMPI detection, respectively, to investigate the multiplet state distributions. Unfortunately, the agreement between these two sets of measurements was poor. Matsumi and Kawasaki [10] later repeated their measurements under conditions of lower ion density and improved their agreement with the results of Huang and Gordon (see Table 1). The O$^{(3)P}$ fragments with $J = 0$ cannot be aligned, and the O$^{(3)P_0}$ images may therefore be fitted to the well-known expression

$$I(\theta) = \frac{1}{4\pi} (1 + \beta P_2(\cos \theta)).$$

(6)
This yields a $\beta$ parameter of $1.94 \pm 0.51$, consistent with the expected value of 2 for a pure parallel transition. We have neglected alignment of the $J = 1$ and $J = 2$ $O(3P)$ photofragments in our analysis of the branching ratios, but examination of the ‘effective’ $\beta$ parameters for these states found by fitting the images to Equation (6) implies that the error introduced by this approximation is less than 10% and lie within our measurement uncertainty.

Branching ratios were determined from the integrated intensities of images recorded at fixed probe wavelengths centred at the peak of the Doppler lineshape for the photofragment of interest. Integrated intensities for each image were obtained by summing the pixel intensities over the region of the images containing appreciable ion signal, with care being taken to ensure that the same region was used for each $J$ state. The intensity of the probe laser was kept low in order to preclude any saturation effects, and two different laser intensities were used in order to check for consistency. The experiment was repeated a number of times so that error estimates could be made. The resulting branching ratios are shown in Table 1. Our results are also in good agreement with the previous measurements of Huang and Gordon, and Matsumi and Kawasaki. The experimental results will be compared with the predictions of theory in Section 4.

<table>
<thead>
<tr>
<th>$J$</th>
<th>Huang et al. LIF (225 nm)</th>
<th>Matsumi et al. REMPI (225 nm)</th>
<th>This study 226 nm</th>
<th>This study 200 nm</th>
<th>Model Adiabatic</th>
<th>Model Diabatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0±0.6</td>
<td>2.4±0.6</td>
<td>1.8±0.3</td>
<td>1.9±0.5</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>1</td>
<td>6.0±0.8</td>
<td>12±4</td>
<td>9.0±1.4</td>
<td>10.4±1.4</td>
<td>0</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>93.1±1.2</td>
<td>86±5</td>
<td>89.2±1.4</td>
<td>87.8±1.8</td>
<td>100</td>
<td>55</td>
</tr>
</tbody>
</table>

3.2. $O(1D_2)$ alignment
As described in Section 2.1, crushed and sliced velocity map images were acquired in four experimental geometries (HH$_c$, HV$_c$, HH$_o$, and HV$_o$) using two different (2+1)REMPI schemes consistent. Since the two schemes have different sensitivities to product angular momentum alignment, this provides further reassurance that neglect of alignment does not have a significant effect on the results of our analysis. Our results are also in good agreement with the previous measurements of Huang and Gordon, and Matsumi and Kawasaki. The experimental results will be compared with the predictions of theory in Section 4.
for REMPI via the $^1P_1$ state there are sizeable contributions from higher order terms. Also, from a polarisation point of view, the HV, and HV$_o$ geometries are equivalent, and should give rise to identical angular distributions in the images. This is seen to be the case when comparing the images in the second and fourth columns of Figure 3.

The appearance of the images may also be explained on a more intuitive level as follows. The photolysis laser is polarised in the 'up-down' direction relative to the images on the page. For a pure parallel transition, parent O$_2$ molecules in our randomly oriented molecular beam whose bond axis has an appreciable component in this direction will be preferentially dissociated, and we therefore expect maximum intensity at the top and bottom of the images. This is clearly seen to be the case in all of the HV geometries. The ionisation (and therefore detection) probability depends on the relative orientation of the photofragment angular momentum, J, and the probe laser polarisation. If J is randomly oriented then the detection efficiency is uniform for all scattering angles. However, if J is polarised (aligned or oriented) in some way relative to the photofragment velocity, the detection efficiency with a probe laser of fixed polarisation will depend on the scattering angle. To illustrate this, consider the crushed image recorded in the HH$_o$ geometry via the $^1P_1$ state. For this probe transition, detection sensitivity is highest when J is parallel to the polarisation vector of the probe light. The extreme top and bottom of the image corresponds to products recoiling along the pump (and probe) polarisation vectors, and the almost complete lack of signal in these regions of the image indicates that J for these products is very strongly polarised perpendicular to this direction. As we shall see, the full analysis reveals that J is indeed strongly polarised in a direction perpendicular to the recoil velocity. The appearance of the remaining images may be rationalised using similar arguments.

These considerations can be put on a more quantitative basis by comparing the observed angular distributions in the images with those that would be observed for products formed in just one of the three possible m($=M_J$) states, i.e. m = 0, 1, 2. The observed angular distribution $I_m(\theta)$ for a given m state, where $\theta$ denotes the scattering angle relative to the photolysis polarisation vector $\epsilon$, and $\Theta$ denotes the angle of the photofragment angular momentum J relative to the probe polarisation vector, may be written as:

$$I_m(\theta, \Theta) = I_{\text{diss}}(\theta) F_{m, \text{det}}(\Theta),$$

where $F_{m, \text{det}}(\Theta)$ is a detection function that depends on the m state and detection scheme as well as on the angle $\Theta$. The appropriate functions for the two REMPI transitions used in this study have been determined by Dylewski et al. [16], and are reproduced below.

$$F_{0,1P_1D} = \frac{3}{4} \frac{3}{10} \cos^2 \Theta - \frac{9}{20} \cos^4 \Theta,$$
$$F_{1,1P_1D} = \frac{7}{10} \frac{3}{5} \cos^2 \Theta + \frac{3}{10} \cos^4 \Theta,$$
$$F_{2,1P_1D} = \frac{13}{40} + \frac{3}{4} \cos^2 \Theta - \frac{3}{40} \cos^4 \Theta,$$
$$F_{0,2P_1D} = 3 \cos^2 \Theta - 3 \cos^4 \Theta,$$
$$F_{1,2P_1D} = \frac{1}{2} + \frac{3}{2} \cos^2 \Theta + 2 \cos^4 \Theta,$$
$$F_{2,2P_1D} = \frac{1}{2} - \frac{1}{2} \cos^4 \Theta. \quad (8)$$

The resulting $I_m(\theta)$ for photofragments with $\beta = 2$ are shown in Figure 4. Comparison of these functions with the images in Figure 3 indicates a high population in m = 0, i.e. J polarised perpendicular to $\nu$, with some contribution from m = 1, and little contribution from m = 2.

In the full analysis described in Section 2, it was found that good fits to the data could be obtained with $\beta$ set to a value of 2 (i.e. assuming a pure parallel excitation). This eliminates all alignment parameters apart from $a^0_0(\|\|)$ and $a^0_0(\|\|)$ from the analysis. Fits were also carried out in which $\beta$ was allowed to vary and all alignment parameters were allowed to be non-zero, but the use of so many fitting parameters seemed poorly justified when the treatment did not yield significantly better fits to the data.

Simultaneous fits were carried out to all crushed and sliced images and to various combinations of subsets of the images in order to establish the errors on the fits. Fitting to the crushed images was very reliable, and virtually independent of the particular images chosen. Fitting to the sliced images was much less reliable, with a significant variation in the alignment.
parameters returned from fits using different combinations of geometries. This is almost certainly due to the fact that the idealised fitting equations for sliced images described in Section 2, which assume an infinitely thin slice through the scattering distribution, do not provide a sufficiently accurate description of the rather more imperfectly sliced experimental images. For this reason we report only the alignment parameters determined from fitting the crushed images: $a_0'(||) = -0.80 \pm 0.04$ and $a_0''(||) = 0.14 \pm 0.02$. These values correspond to strong alignment of $\mathbf{J}$ perpendicular to $\mathbf{v}$, in accord with our more qualitative consideration of the images above.

The alignment parameters may be used to calculate the density matrix for the $\text{O}(1\text{D})$ product, and therefore the $m (=M_J)$ state populations (these are simply the diagonal elements, $\rho_{mm}$ of the density matrix). These $m$-state populations determined from the experimental data are given in Table 2 and plotted in Figure 5, together with a reconstruction of the angular distribution of $\mathbf{J}$. As inferred from our previous consideration of detection functions, within our experimental uncertainties most of the photofragments are born in $m = 0$, with some contribution from $m = 1$ and almost no contribution from $m = 2$.

These results will be compared with the predictions of theoretical models in Section 4.

### 3.3. $\text{O}(1\text{D}_2)$ photofragments from vibrationally excited $\text{O}_2$

Images recorded in the one-laser HHc geometry following photodissociation of vibrationally excited $\text{O}_2$ at 203.815 nm and 205.473 nm are shown in Figure 6(a). Together with the photon energy and the bond dissociation energy of $\text{O}_2$, the degree of vibrational excitation in the parent $\text{O}_2$ determines the total energy available to the photofragments, and hence the recoil velocity of the the $\text{O}(1\text{D})$ atom. The mixture of vibrational states produced in the discharge source therefore gives rise to an image consisting of concentric rings, with the intensity of each ring reflecting the population of the corresponding $\text{O}_2$ vibrational state in the molecular beam (and also its photodissociation cross-section at the wavelength of interest), and the spacing between rings reflecting the vibrational spacing in $\text{O}_2$. Vibrational states from $v = 6$ to $v = 12$ make a significant contribution to the experimentally measured images.

Figure 6(b) shows the total kinetic energy release distributions for the detected products, and reveals the relative contribution to the images from the different populated vibrational states in the $\text{O}_2$ parent molecule. The parent vibrational distributions extracted from these data are shown in Figure 6(c). The marked difference for the two photolysis wavelengths arises from wavelength-dependent variations in the absorption cross-sections for the different vibrational states. Transition dipole moments for the $B \rightarrow X$ transition in $\text{O}_2$ are known [17], and a relatively straightforward Frank–Condon-based calculation yields the photodissociation cross-section as a function of wavelength and vibrational state. These are shown in Figure 6(d), and show significant variations between the two photolysis wavelengths of interest, in line with our experimental data.

While the quality of the data is not high enough to carry out a full analysis, comparison of the images with those recorded in the HHc geometry for 157 nm photolysis of $\text{O}_2$ in its vibrational ground state indicates a similar strong alignment of $\mathbf{J}$ perpendicular to $\mathbf{v}$. This suggests that provided dissociation occurs via the $B$ state, angular momentum alignment in the

<table>
<thead>
<tr>
<th>$m$</th>
<th>Population</th>
<th>Error</th>
<th>$\Psi_0$</th>
<th>$\Psi_{\pm 1}$</th>
<th>$\Psi_{\text{avg}}$</th>
<th>Diabatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>73</td>
<td>+6, -1</td>
<td>12</td>
<td>49</td>
<td>36</td>
<td>89</td>
</tr>
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<td>1</td>
<td>23</td>
<td>+6, -4</td>
<td>34</td>
<td>50</td>
<td>44</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>+2, -3</td>
<td>54</td>
<td>1</td>
<td>19</td>
<td>0</td>
</tr>
</tbody>
</table>

*Table 2. Measured and calculated $m$ state populations (expressed as percentages) for the $\text{O}(1\text{D}_2)$ photofragments following 157 nm photodissociation of $\text{O}_2$. For the adiabatic model, the results for the lowest $\Omega = 0^+$, $\pm 1$ states are given, together with their statistical average.*
O(1D) photofragments is largely independent both of parent vibrational state and of photolysis wavelength. Similar strong alignment was also seen in a study by Eppink et al. [4] in which the B state was accessed by a two-photon transition from the ground state.

4. Discussion

To first order, it is straightforward to explain the observed alignment in the O(1D) fragments if we assume the B state to be a pure \( S \) state with \( \Lambda = |M_L| = 0 \), where the bond axis is the axis of quantisation. This state dissociates (transforming the bond axis onto the photofragment recoil axis) to give an O(3P) and an O(1D) atom, which must either have \( M_L(a) = 0 \), \( M_L(b) = 0 \) or \( M_L(a) = \pm 1 \), \( M_L(b) = \mp 1 \) (for the remainder of the paper, quantum numbers denoted \( a \) and \( b \) refer to the O(3P) and O(1D) fragments, respectively). As we shall show later using a diabatic model of the dissociation, the major contribution to the B state is from the former of these states, and the O(1D) therefore has \( M_L = 0 \). By virtue of being a singlet state, it also has \( M_S = 0 \), and therefore \( M_J = m = 0 \), i.e. \( J \) is polarised perpendicular to the recoil axis.

This is a very simplistic model of the photodissociation process, and our data show that while O(1D) is preferentially formed in \( m = 0 \), there is also appreciable population in other \( m \) states, primarily \( m = 1 \). The above model also offers no explanation for the spin–orbit populations in the O(3P) coproduct. Obtaining a more rigorous understanding of the dissociation dynamics leading to the observed O(1D) alignment and O(3P) spin–orbit populations requires a detailed consideration of the molecular electronic states involved in the excitation process and their evolution into the atomic product states.

We first consider the molecular states. In a Hund’s case (a) treatment, these may be defined by the set of quantum numbers \( |\Lambda S \Sigma \Omega \rangle \). For the \( \text{O}_2 \) molecule in its electronic ground state, \( \text{X}^3\Sigma_g^- \), the quantum number \( \Lambda \), denoting the projection of the orbital angular momentum \( L \) onto the internuclear axis, is equal to zero. The total spin is \( S = 1 \), with the projection onto the axis given by \( \Sigma = 0, \pm 1 \). \( \Lambda \) and \( \Sigma \) couple together to give a total spin and orbital angular momentum projection of 0, \( \pm 1 \). \( \Omega \) is defined as the absolute value.
of this projection, and therefore takes values $\Omega = 0, 1,$ with a 1:2 weighting of populations (i.e. $p(0) = 1/3$, $p(1) = 2/3$). Finally, for a molecule with $\Lambda = 0$, $J$ is given by coupling of the nuclear rotation ($N=1$ for the rotational ground state) with the electronic spin ($S=1$ for a triplet state) to give $J = 0, 1, 2$. These three states are populated according to their statistical weights, $2J + 1$.

On excitation to the $B^3\Sigma_u^-$ state, the quantum numbers $\Lambda$, $S$, $\Sigma$, and $\Omega$ are unchanged. If we assume the sudden recoil limit for dissociation from the $B$ state, i.e. that the dissociation occurs on a faster timescale than molecular rotation, we also do not need to consider changes in $J$. In the Frank–Condon region of the excitation, the molecular electronic states (calculated by diagonalising the Coulomb Hamiltonian $\hat{H}_{\text{Coul}}$ within the Born–Oppenheimer approximation) are well separated in energy, and spin–orbit coupling is negligible. However, on dissociation, the adiabatic Born–Oppenheimer states correlating with the $\Omega(1^L D) + \Omega(3^L P)$ limit become degenerate, and are mixed by the spin–orbit coupling Hamiltonian $\hat{H}_{\text{SO}}(R)$, where $R$ is the interatomic distance. For large separations, $\hat{H}_{\text{SO}}(R)$ approaches the $\Omega(3^L P)$ spin–orbit coupling energy.

The $\Omega(1^L D)$ alignment and $\Omega(3^L P)$ spin–orbit populations are determined as the system passes through the ‘spin–orbit coupling region’ linking the molecular states to the atomic states. The probability of eliciting transitions between spin–orbit states in this region may be related to the Massey parameter [18]

$$\zeta = \frac{\Delta E_{\text{SO}} a}{hv},$$

where $\Delta E$ is the spin–orbit splitting, $a$ is a distance parameter representing the extent of the spin–orbit coupling region, and $v$ is the velocity of the system as it passes through the spin–orbit coupling region. A Massey parameter with a value much less than unity (i.e. the time taken for the system to pass through the coupling region is much shorter than the characteristic time associated with spin–orbit coupling) predicts diabatic dynamics, while a value much greater than unity would predict adiabatic dynamics. We can use as an approximate value for $v$ the maximum relative velocity of the $\Omega(1^L D)$ and $\Omega(3^L P)$ fragments. This may be calculated from conservation of energy to be 4434 m s$^{-1}$. The spin–orbit splittings for the $J=0$–1 and $J=1$–2 levels of $\Omega(3^L P)$ are 0.00852 and 0.01962 eV, respectively, and an inspection of the potential energy curves for $O_2$ indicates that we may take $a$ to be around 3 a.u. This yields Massey parameters of 0.87 and 2.00 for the two spin–orbit splitting values. There is therefore no clear prediction as to which regime the dynamics of $O_2$ photodissociation should fall into, and we have therefore modelled the dissociation theoretically using both a diabatic and an adiabatic model.

The models used here are based on the work of Singer et al. [19], and have been applied before to several systems, including photodissociation of $O_2$ in the Herzberg continuum [20–22] and photodissociation of $O_2^+$ [23,24]. The diabatic model assumes that the transition through this region is fast, and calculates the product wave functions by projecting the adiabatic Born–Oppenheimer molecular wavefunction onto the atomic fine structure states. In contrast, in the adiabatic model the transition is assumed to be slow, and the fragment wave functions follow from the Hund’s case (c) correlation diagram. The case (c) functions are eigenfunctions of $\hat{H}_{\text{Coul}}(R) + \hat{H}_{\text{SO}}(R)$, labelled by the $\Omega$ quantum number.

### 4.1. Diabatic model

As noted previously in the simplified treatment given at the start of the Discussion, the possible atomic states correlating with a $\Lambda = 0$ molecular $\Sigma$ state are $|M_L(a), M_J(b)\rangle = |\lambda_a, \lambda_b\rangle = |0, 0\rangle, |1, -1\rangle, |1, 1\rangle$. Imposing the symmetry requirements of a $\Sigma^-$ molecular state yields two possible molecular states:

$$\phi_1 = |0, 0\rangle,$$
$$\phi_2 = \frac{1}{2^{1/2}} (|1, 1\rangle + |1, -1\rangle).$$

At long range, the Coulomb interaction between the $\Omega(1^L D)$ and $\Omega(3^L P)$ atoms is dominated by the electrostatic quadrupole–quadrupole interaction $\hat{V}^{(2,2)}$. By determining the eigenfunctions of $\hat{V}^{(2,2)}$ variationally using the functions $\phi_1$ and $\phi_2$ as a basis, we can determine the relative contributions of these two functions to the molecular $B^3\Sigma_u^-$ state on which $O_2$ dissociates. Details of this calculation are given in Appendix 2. The treatment predicts the lowest energy $\Sigma_u^-$ wavefunction, corresponding to the $B$ state, to be $\Psi_1 = 0.94\phi_1 + 0.34\phi_2$. From this result we can immediately predict the $m = M_J$ populations of the $\Omega(1^L D)$ product to be $p(0) = 0.94^2 = 0.89$, $p(1) = 0.34^2 = 0.11$, $p(2) = 0$, in good accord with the experimental results.

To find the $\Omega(3^L P)$ spin–orbit state branching ratios we first need to include the spin part of the molecular wavefunction, $|\Sigma\rangle$, into $\Psi_1$ above. This gives a molecular basis described by the quantum numbers $|\lambda_a, \lambda_b, \Sigma; R\rangle$, with $R$ the atomic separation. The spin of the $\Omega(1^L D_2)$ atom is zero, but we need to include the spin contribution $|\frac{1}{2}, \sigma_a\rangle$ of the $\Omega(3^L P)$ into our representation of the atomic states. Assuming
Russell-Saunders coupling, the atomic spin–orbit states of the \( \text{O}^3P \) can then be represented as

\[
|l_a s_a \rangle_j |o_a o_b \rangle = \sum_{l_a \sigma_a} |l_a \sigma_a \rangle |s_a \rangle |l_a \sigma_a \rangle |o_a o_b \rangle, \tag{11}
\]

where \( |l_a \sigma_a \rangle |s_a \rangle |l_a \sigma_a \rangle |o_a o_b \rangle \) is a Clebsch–Gordan coefficient. The transformation matrix elements between the atomic spin–orbit state basis and the molecular wavefunctions are given by

\[
\langle j_a o_a l_a o_b |l_a \sigma_a \rangle |s_a \rangle |l_a \sigma_a \rangle |o_a o_b \rangle \rangle = \delta_{j_a j_b} \langle j_a \sigma_a |s_a \rangle \langle |l_a \sigma_a \rangle \langle |o_a o_b \rangle \rangle. \tag{12}
\]

The spin–orbit state branching ratios \( p(j_a) \) in the \( \text{O}^3P \) are found by summing the square of the above matrix elements over the quantum numbers \( o_a \) and \( l'_a \), and taking the weighted average over the molecular spin state contributions.

\[
p(j_a) = \frac{1}{3} \sum_{o_a} \sum_{l'_a} \langle |j_a o_a l'_a o_b \rangle \rangle |s_a \rangle |l_a \sigma_a \rangle |o_a o_b \rangle \rangle = \frac{j_a + 1}{9}. \tag{13}
\]

This yields spin–orbit state populations of 0.55 : 0.33 : 0.11 for \( j = 2, 1, 0 \), respectively. The diabatic model predicts that the states are populated statistically. While the diabatic model predicts the \( \text{O}^1\text{D} \) alignment fairly reliably, its predictions for the \( \text{O}^3\text{P} \) spin–orbit populations are in less good agreement with the experimental results.

4.2. Adiabatic model

In the adiabatic model, passage through the spin–orbit coupling region during the dissociation is assumed to be slow, and the \( \text{O}^3\text{P} \) spin–orbit branching ratios follow from the Hund’s case (c) correlation diagram, as published by Huang and Gordon [8]. Both the \( B^1\Sigma_u^+ \) and \( B^3\Sigma_u^+ \) states correlate with the \( ^3P_2 + ^1D \) atomic limit, i.e. all products are formed in the \( \text{O}^1\text{D} \) state, with no population in \( ^3P_1 \) or \( ^3P_0 \). This is in reasonably good accord with the experimental data.

The alignment of the \( \text{O}^1\text{D} \) photofragments is found by determining the asymptotic case (c) functions for the atomic products that correlate with the \( B^3\Sigma_u^+ \) and \( B^1\Sigma_u^+ \) states. There are three \( \Omega = 0^+ \) states correlating with the \( ^3P + ^1D \) limit, and four \( \Omega = 1^- \) states, which we can label by the quantum numbers \( |o_a o_b \rangle = |j_a o_a l'_a o_b \rangle \), with \( o_a + o_b = \Omega \). The three \( \Omega = 0^+ \) functions are:

\[
\begin{align*}
\phi_1 &= |0, 0\rangle, \\
\phi_2 &= (|1, -1\rangle + |-1, 1\rangle)/2^{1/2}, \\
\phi_3 &= (|2, -2\rangle + |-2, 2\rangle)/2^{1/2} \tag{14}
\end{align*}
\]

and the four \( \Omega = 1^- \) states are \(|2, -1\rangle, |1, 0\rangle, |0, 1\rangle, \) and \(|-1, 2\rangle \). As in the diabatic case we determine the contribution of these states to the molecular wavefunctions by determining the eigenfunctions of the electrostatic quadrupole–quadrupole Hamiltonian, \( \tilde{\mathbf{V}}^{(2,2)} \), variationally using these functions as a basis. The lowest energy \( \Omega = 0^+ \) and \( \Omega = 1^- \) functions determined from this treatment are:

\[
\begin{align*}
\Psi_0^+ &= 0.345 \phi_1 + 0.583 \phi_2 + 0.736 \phi_3, \\
\Psi_1 &= 0.118 \langle (2, -1) - | -1, 2 \rangle + 0.697 \langle (1, 0) - | 0, 1 \rangle. \tag{15}
\end{align*}
\]

The function \( \Psi_{-1} \) is found by changing the signs of the \( o_a \) and \( o_b \) quantum numbers in \( \Psi_1 \). The \( \text{O}^1\text{D} \) \( m \)-state populations are found from the squares of the expansion coefficients for \( |o_b| = 0, 1, 2 \) in these wavefunctions, with a weighted average taken over \( \Psi_0 \) and \( \Psi_{\pm 1} \). This gives populations of 0.36, 0.44 and 0.19 for \( m = 0, 1, 2 \), in poor agreement with the experimentally observed alignment.

4.3. Comparison with experimental results

Experimental data obtained over the range of excess energies from 0.08–1.0 eV (Figure 2) show strong alignment of the \( \text{O}^1\text{D} \) fragment, with population predominantly in the \( m = 0 \) sublevel. The diabatic model shows good agreement with the measured \( \text{O}^1\text{D} \) alignment, but does not provide a satisfactory prediction of the \( \text{O}^3\text{P} \) spin–orbit state branching ratios. Given the near-unity values of the Massey parameter for dissociation at this wavelength (see previous discussion), it is unsurprising that the dissociation exhibits mixed diabatic/adiabatic dynamics. The good agreement of the diabatic model with the observed \( \text{O}^1\text{D} \) alignment may arise because the \( S = 0 \) nature of the atom means that it is not influenced by spin–orbit interactions in the spin–orbit recoupling zone. Recently, Lambert et al. [3] have measured the branching ratios at shorter wavelengths than in the present study. The populations for the \( J = 0, 1, 2 \) spin–orbit states were found to be 0.13 ± 0.18, 0.32 ± 0.13, 0.56 ± 0.15 at 124.4 nm, and 0.10 ± 0.07, 0.24 ± 0.90, 0.66 ± 0.11 at 151.7 nm. The results at 124.4 nm are in virtually perfect agreement with the predictions of the diabatic model, and if the populations measured at these two wavelengths are compared with our measurements at 200 and 226 nm, it appears that there is essentially a smooth transition from mixed diabatic/adiabatic dynamics at longer wavelengths to pure diabatic dynamics at shorter wavelengths.

In contrast to the predictions of the diabatic model, the adiabatic model shows poor agreement with the measured \( \text{O}^1\text{D} \) alignment, but better agreement with
the $O(3P)$ spin–orbit state branching ratios. The adiabatic model takes better account of spin–orbit coupling effects, but is still unable to predict the small amounts of population observed in $O(3P_1)$ (10%) and $O(3P_0)$ (2%). These populations presumably arise from non-adiabatic transitions occurring during the dissociation process. Such non-adiabatic effects have been discussed by Huang and Gordon [8] using the Massey criteria and the Landau–Zener and Demkov models.

Recently, Vroonhoven and Groenenboom [20,21] have carried out semiclassical calculations to predict $O(3P)$ polarisation in the $O(1D)+O(1D)$ channel following photodissociation of $O_2$ in the Herzberg continuum. This is a more complicated case to treat than the $O(1D)+O(3P)$ channel, having 81 microstates to include as opposed to 45 and the additional complication of indistinguishable atoms. A similar semiclassical calculation for the $O(3P)+O(1D)$ channel following photodissociation in the Schumann–Runge continuum should help to solidify our understanding of the dissociation process.

5. Conclusions
We have used the velocity-map imaging technique to investigate the direct photodissociation of $O_2$ via the $B^3Σ_u^+$ state in the well-known Schumann–Runge continuum. Dissociation occurs via a pure parallel transition. Both VUV photodissociation of $O_2(v=0)$ at 157 nm, and UV photodissociation of $O_2(v=6–11)$ at 203.8 and 205.5 nm, yields highly polarised $O(1D_2)$ photofragments. The $O(1D_2)$ fragments are formed with their electronic angular momentum $J$ polarised preferentially perpendicular to their recoil velocity, i.e. in the $m=0$ magnetic sublevel. Spin–orbit state branching ratios for the $O(3P)$ fragment were also measured, and found to be in good agreement with previously published measurements. The fragmentation process has been modelled using a diabatic and an adiabatic treatment of the dissociation. The diabatic model was able to provide a satisfactory model of the $O(1D)$ alignment, but failed to model the $O(3P)$ spin–orbit populations, while the reverse was true for the adiabatic model. 

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References
Appendix 1. Analytical expressions for velocity-map images for analysis of photofragment angular momentum alignment

The alignment/orientation is described using the formalism developed by Rakitis and Zare [12]. In this formalism, the spatial distribution of the photofragment angular momentum \( \mathbf{J} \) in the molecular frame is expanded as a sum over modified spherical harmonics \( C_n^m(\theta, \phi) = (4\pi/(2n + 1))^{1/2} y_n^m(\theta, \phi) \), where \( y_n^m(\theta, \phi) \) are the standard spherical harmonics.

\[
P(\theta, \phi) = \sum_{k=0}^{M} \sum_{q=-k}^{k} A_{kl}^{(k)} y_n^m(\theta, \phi) 
\]

Here, \( \theta \) and \( \phi \) are the polar angles relative to a z axis lying along the photofragment velocity vector \( \mathbf{v} \) and an x axis lying in the plane of \( \mathbf{v} \) and the photolysis polarisation vector \( \mathbf{e}_{\text{phot}} \).

It is therefore valid only for a fixed angle \( \theta \) between these two vectors. In order to obtain a general expression for the angular momentum polarisation that includes the angular distribution of the photofragments, we can separate Equation (16) into a contribution from pure parallel transitions, a contribution from pure perpendicular transitions, and interference terms between the two. To achieve this separation we introduce a set of alignment parameters \( A_{kl}^{(k)}(\text{pol}) \), which are related to the \( A_{kl}^{(k)} \) as follows:

\[
A_{0}^{(k)} = [(1 + \beta) \cos^2 \theta_0 a_0^{(k)}(\|) + (1 - \beta/2) \sin^2 \theta_0 a_0^{(k)}(\perp)]/[1 + \beta P_2(\cos \theta_0)], \quad \text{(17)}
\]

\[
A_{1}^{(k)} = \sin \theta_0 \cos \theta_0 a_0^{(k)}(\|, \perp)/(1 + \beta P_2(\cos \theta_0)), \quad \text{(18)}
\]

\[
A_{2}^{(k)} = (1 - \beta/2) \sin^2 \theta_0 a_0^{(k)}(\perp)/[1 + \beta P_2(\cos \theta_0)], \quad \text{(19)}
\]

The \( a_0^{(k)}(\|) \) describe contributions to the alignment from processes involving pure parallel transitions from the ground state and the \( a_0^{(k)}(\perp) \) from perpendicular transitions, with the \( a_0^{(k)}(\|, \perp) \) arising from interference between the two types of process. For terms up to \( k = 2 \), the details of this separation are all described in [12]. At this point we have an expression for the molecular frame angular momentum alignment (Equation (14) of [12] for moments up to \( k = 2 \)). To obtain an expression for the measured distribution, we need to correct each term in this equation for the detection sensitivity, which will depend on details of the experiment such as the REMPI transition chosen to detect the fragments and the polarisation of the probe light. For comparison with experimental data, we also need to transform the expression into a laboratory frame. For imaging experiments the most convenient lab frame has \( z \) lying along the time-of-flight direction, and \( x \) in the plane of \( \mathbf{v} \) and the photolysis polarisation. We can then define three sets of angles:

1. \((\Gamma, 0)\) define the photolysis polarisation relative to the lab z axis.
2. \((\Delta, \Phi)\) define the probe polarisation relative to the lab z axis.
3. \((\Omega, \Theta)\) define the product velocity \( \mathbf{v} \) relative to the lab z axis.

These angles define the four experimental geometries described in Figure 3. After some manipulation, which involves using results from above, determining expressions for transforming between the lab frame and molecular frame coordinates, and extending the expressions in [12] to include terms up to \( k = 4 \), the final expression for the measured signal intensity in terms of the \( a_{kl}^{(k)}(\text{pol}) \) parameters is:

\[
I = 1 + c \beta C_2(\gamma) \\
+ s_1 \left\{ (1 - \beta/2) a_0^{(1)}(\perp) C_{10}(\delta) C_{0}\gamma + 2^{1/2} \text{Re}[a_1^{(1)}]\right\} \]

\[
+ C_{11}(\delta) \cos \phi + c(8/3)\gamma^{1/2} \text{Im}[a_1^{(2)}] C_{11}(\delta) C_{21}(\gamma) \sin \phi \]

\[
+ s_2 \left\{ (1/3)(1 + \beta) a_0^{(2)}(\perp) + 2(1 - \beta/2) a_0^{(2)}(\perp) C_{20}(\delta) + c(2/3) \right\} \]

\[
+ c(8/3)\gamma^{1/2} \text{Re}[a_1^{(2)}] C_{21}(\delta) C_{21}(\gamma) \cos \phi + (8/3)\gamma^{1/2} \text{Im}[a_1^{(2)}] C_{21}(\delta) \]

\[
\times C_{21}(\gamma) \sin \phi + c(32/3)\gamma^{1/2} \left\{ (1 - \beta/2) a_0^{(2)}(\perp) C_{22}(\gamma) \cos 2\phi \right\} \]

\[
+ s_3 \left\{ (1 - \beta/2) a_0^{(2)}(\perp) C_{30}(\delta) C_3(\gamma) + 2^{1/2} \text{Re}[a_1^{(3)}] C_{31}(\delta) \right\} \]

\[
+ C_{11}(\delta) \cos \phi + c(8/3)\gamma^{1/2} \text{Im}[a_1^{(3)}] C_{31}(\delta) C_{21}(\gamma) \sin \phi \]

\[
+c(32/3)\gamma^{1/2} \left\{ (1 - \beta/2) a_0^{(3)}(\perp) C_{22}(\gamma) \cos 2\phi \right\} \].

(20)

A number of quantities appearing in this equation require explanation:

1. The angles \( \gamma, \delta, \phi \) and \( \phi \) are determined from \( \cos \gamma = \cos \Omega \cos \Gamma + \sin \Omega \sin \Gamma \cos \Theta \), \( \cos \delta = \cos \Omega \cos \Delta + \sin \Omega \sin \Delta \cos (\Theta - \Phi) \), \( \cos \phi = \sin^2 \Omega \cos \Delta + \sin \Omega \sin \Delta \cos \Phi - \sin \Omega \cos \Omega \sin \Delta \cos \Gamma \phi \sin \Theta \), \( \sin \phi = \sin \Omega \sin \Delta \sin \Phi - \sin \Omega \sin \Delta \sin \Theta \), \( \sin \phi = \sin \Omega \sin \Delta \sin \phi - \sin \Omega \cos \Omega \sin \Delta \cos \Theta \), \( \sin \phi = \sin \Omega \sin \Delta \cos \Phi + \sin \Omega \cos \Delta \sin \Phi \).

2. The \( s_k \) are REMPI sensitivity parameters that depend on the \( J \) values of the initial, intermediate and final states in the REMPI transition used to ionise the photofragments [13–15].

3. \( c \) is a constant equal to 1 for experimental geometries in which the pump laser is linearly polarised, and \( 1/2 \) for geometries in which the pump laser is circularly polarised.

Equation (20) describes the full 3D distribution of the detected photofragments. To obtain an expression for a crushed velocity-map image recorded in a particular experimental geometry, we simply substitute in the appropriate values of the angles \( \Gamma, \Delta \) and \( \Phi \) to describe the experimental geometry.
where the atomic quadrupole operators for atom \(a\) defined in atomic units by
\[
\hat{Q}_{2,m}^{(a)} = - \sum_i (r_i \times \mathbf{C}_{2m}(\theta_i, \phi_i)),
\]
\[m = -2, 0, 2\]
In the above, \(C_{0a}\) is a Racah normalised spherical harmonic, and \(r_i, \theta_i,\) and \(\phi_i\) are the spherical polar coordinates of the electrons in the atomic frame. The matrix elements of \(\hat{Q}_{2,m}^{(a)}\) are related through the Wigner–Eckart theorem:
\[
\langle l_a | \hat{Q}_{2,m}^{(a)} | l_a \rangle = (-1)^{l_a + l_b - m} \begin{pmatrix} l_a & l_b & l_c \\ -m & -l_b & m \end{pmatrix} (l_a || 2 | l_b) \times \begin{pmatrix} l_a & 2 \\ -m & l_b \end{pmatrix} (l_a || 2 | l_b),
\]
where \((\ldots)\) is a 3\(j\) symbol and \(\langle l_a || 2 | l_b \rangle\) is the reduced quadrupole moment of atom \(a\). Since only the signs of these moments are essential in this derivation, it is sufficient to derive their value in a one-determinant approximation of the atomic wavefunction. Employing the methods used to derive this quantity for the \(O(1D_2)\) atom in [26], the reduced quadrupole moments for \(O(2D_2)\) and \(O(2P)\) are found to be:
\[
\langle l_a = 2 | 2 | l_b \rangle = -(14/5)^{1/2} (r^2),
\]
\[
\langle l_a = 1 | 2 | l_b \rangle = (6/5)^{1/2} (r^2),
\]
where \((r^2)\) is the expectation value of \(r^2\) for an oxygen 2\(p\) orbital. The matrix elements of \(\hat{V}^{(2,2)}(R)\) in the atomic basis \(|l_a \lambda_a \rangle \langle l_b \lambda_b|\) are found by substituting Equation (25) into Equation (23).
\[
\langle l_a | \hat{Q}^{(2,2)}(R) | l_a \lambda_a \rangle = \sum_{m=-2}^{2} \langle l_a \lambda_a | l_b \lambda_b | 2, m, 2, -m | 4, 0 \rangle \times \begin{pmatrix} l_a & 2 \\ -m & l_b \end{pmatrix} (l_a || 2 | l_b) \times \begin{pmatrix} l_a & 2 \\ -m & l_b \end{pmatrix} (l_a || 2 | l_b),
\]
where \(m = \lambda_a - \lambda_b\). The adiabatic model requires the matrix elements
\[
\langle j_a | \hat{Q}^{(2,2)}(R) | j_a \rangle = \langle j_a | 2 | j_a \rangle = \langle j_a | 2 | j_a \rangle (\ldots) + \langle j_a | 2 | j_a \rangle (\ldots) + \ldots + \langle j_a | 2 | j_a \rangle (\ldots),
\]
where the last factor is a 6\(j\) symbol.