FINAL REPORT

Imaging Orbital Polarization *Grant GR/S69313/01*

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1. Background

Photodissociation often involves bond fission, leading to the generation of open shell atomic or radical fragments. As a result, more than one molecular electronic state necessarily converges to the (open shell) photofragment channel of interest, and the task of assigning which parent molecular electronic states are populated during photodissociation can be a difficult one. Obtaining a complete understanding of molecular photodissociation requires determination of quantum state populations, state-to-state cross-sections, angular scattering distributions, and product angular momentum polarizations (both electronic and rotational) [1, 2]. The topic of the original proposal, and of this final report, is the measurement of the electronic fine-structure cross-sections (or populations), state-resolved angular distributions, and angular momentum polarization in the open shell fragments of the photodissociation of atmospherically important molecules [3].

In the following we describe how it is possible to measure the relationship between the direction in which the photofragments are scattered and the details of their internal electronic angular momenta. The study of orbital and spin polarization of the product photofragments has become widely recognized as providing detailed insights into molecular photodissociation dynamics. Polarization of the photofragment angular momenta is a manifestation of non-equilibrium populations of the corresponding magnetic sublevels, and is usually characterized at a theoretical level by the state multipole moments of the M-state distribution of the atomic products [4, 5]. The electronic angular momentum polarization contains a very detailed 'travelogue' of the dissociation or scattering process, revealing which molecular orbitals are occupied by the (asymptotically unpaired) electrons during a chemical event. Although polarization effects might appear a somewhat esoteric feature of the chemical process, we demonstrate in the following summary of our research that they are potentially of very significant practical utility in helping to elucidate the photodissociation mechanism.

2. Key advances

Technical achievements:

During the course of the proposal we have completely redesigned and rebuilt our ion-imaging machine, and installed a new Nd:YAG pumped dye laser system. Both of these became fully operational very quickly after the start of the grant, which has had a significant positive impact on productivity during the three year period under review. A further important development has centred around improvements to our data analysis procedures. The ion image is a two-dimensional projection of the full three-dimensional (3D) velocity distribution of interest. A number of tried-and-tested routines are available which allow direct inversion of the image to obtain the velocity distribution. However, these all require the velocity distribution to possess cylindrical symmetry. We have devised an alternative general procedure, based on a Fourier moment analysis of the ion-image [6], which has proved very effective, and this has been modified and updated to include the latest quantum mechanical expressions for the dissociation density matrix [7]. We have chosen the Fourier moment analysis of the 'crushed' images in preference to using 'slice' imaging [9], since our simulations suggest that slice imaging is generally unsuitable in cases where angular momentum polarization effects are to be extracted over a broad range of photofragment velocities, as is the case in the majority of studies described below.

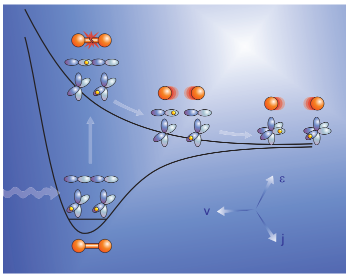

Figure 1: Illustration of the origin of angular momentum polarization in the dissociation of a simple diatomic molecule. This picture is taken from the cover of PCCP, in which our Invited Article on the subject was published [8].

Another extremely important aspect of the research has been our participation in the development of models of atomic polarization in molecular photodissociation. Although we would not wish to claim the credit for developing these theories ourselves, we believe that our experimental results have inspired a number of theoreticians to work on aspects of the important problems described below. This work comprises the development by our collaborators of: (i) methods for visualizing angular momentum distributions in a rigorous quantum mechanical fashion [10]; (ii) fast dissociation (diabatic) models of angular momentum polarization in molecular photodissociation, accommodating both the presence [11] or absence [12] of spin polarization; and finally (iii) the refinement of a long-range interaction model and its application to a number of systems described here [7, 11]. Our work has also provided motivation for a number of theoretical studies [13, 14], most notably concerning the photodissociation of ozone [15].

The experiments described below highlight some of the specific achievements of the research undertaken over the last three years.

$N_2O + h\nu \rightarrow N_2(X^1\Sigma_g^+) + O(^3P_J)$:

Our ion imaging study of the velocity and angular momentum alignment distributions of the $\mathrm{O}(^3\mathrm{P}_J)$ products of $\mathrm{N_2O}$ photolysis at 193 nm commenced before the start of the proposal [12], but several models have been used to help interpret our results since the original publication. The quantum yield for the triplet channel, originally estimated at a few percent [12], has also subsequently been measured by Nishida *et al.* to be $\sim$0.005 [16]. The velocity and spatial anisotropy distributions we determined indicated that around 60% of the available energy appears in product translation. The remainder is released into internal excitation of the $\mathrm{N_2}$ cofragment, with internal energy distributions that are reminiscent of those observed for the primary photodissociation channel leading to singlet oxygen [12]. The measured $\mathrm{O}(^3\mathrm{P}_J)$ alignment parameters were interpreted in terms of the diabatic dissociation models [12, 17], which suggested preferential population of $M_L = 0$ states, and an electron density distribution peaking perpendicular to the direction of the breaking bond. Some spin polarization during dissociation was also observed [17]. This is consistent with dissociation on a triplet surface of Σ^- symmetry, the most likely candidate correlating with ground state products being the asymptotic $^3\Sigma^-(^3A'')$ surface. There are several possible routes to this surface, including direct excitation to the triplet state, or intersystem crossing from the singlet state responsible for production of $\mathrm{O}(^1\mathrm{D}_2)$. In the light of the similarities between the speed and angular distributions arising from the singlet and triplet channels, the latter mechanism seems the most likely. Finally, it should be noted that this system provides a very interesting comparison with the photodissociation of the isovalent OCS molecule, discussed further below.

$SO_2 + h\nu \rightarrow SO(X^3\Sigma^-) + O(^3P_J)$:

The 193 nm photodissociation of $\mathrm{SO_2}$ was also studied, and the dependence of the ion images on the linear polarization of pump and probe radiation used to determine the electronic angular momentum alignment of the recoiling, state-selected atoms [11]. The system was of particular interest in that a variety of dissociation pathways had been proposed, involving either internal conversion to the ground state, intersystem crossing to a nearby $2^3\mathrm{A}'$ state, or adiabatic dissociation *via* the $3^1\mathrm{A}'$ state [18]. Our polarization measurements were able to help shed light on the true dissociation mechanism. The polarization data for $J = 1$ and 2 were used to estimate the state multipole moments of the O-atom electron spin and orbital angular momenta. These revealed that both sources of O-atom electronic angular momentum are polarized [11, 17]. It was shown that the spin polarization could either arise from exit channel couplings, or be a manifestation of the participation of triplet states in the dissociation. The angular dependence of the potential energy in the exit channel was examined using long range quadrupole-dipole and quadrupole-quadrupole interaction terms, from which molecular frame multipole moments of the orbital angular momentum of the recoiling O-atoms were calculated. Comparison with the experimentally derived multipole moments suggested that the most likely dissociation pathway was that involving internal conversion to the ground state, with electron spin polarization arising from spin-orbit interactions in the long-range recoupling zone of the exit channel [11, 17].

$O_2 + h\nu \rightarrow O(^3P_J) + O(^3P_{J'})$:

This important diatomic system provided an opportunity to compare our experimental results with more sophisticated (but still not exact) theory [19]. Under the jet-cooled conditions employed, absorption of $\mathrm{O_2}$ at 193 nm is believed to be dominated by excitation into the Herzberg continuum [8]. The experimental translational anisotropy and polarization data were compared with theoretical calculations at 193 nm and other wavelengths. Semi-classical calculations performed by van Vroonhoven and Gröenenboom [20] were used to estimate the alignment parameters arising from incoherent excitation and dissociation, and these were shown to agree qualitatively well with the available experimental data. Following the work of Alexander *et al.* [21], orientation and alignment parameters arising from coherent excitation and dissociation were modelled more approximately by estimating phase differences generated subsequent to dissociation *via* competing adiabatic pathways leading to the same asymptotic products. These calculations provided support for the view that large values of the coherent alignment moments, but small values of the corresponding orientation moments, could arise from coherent excitation of (and subsequent dissociation *via*) parallel and perpendicular components of the Herzberg I, II, and III transitions [8, 19].

$NO_2 + h\nu \rightarrow NO(X^2\Pi) + O(^3P_J)$:

In this study [22] we provided information about the $O(^3P_J)$ products subsequent to photolysis of NO_2 at 308 nm, and at the probe wavelength of 226 nm. The atomic speed distributions were used to provide information about the internal quantum state distribution in the NO co-products. The data were found to be consistent with an inverted NO vibrational quantum state distribution, and thereby pointed to a dynamical, as opposed to a statistical dissociation mechanism subsequent to photodissociation at 308 nm. Surprisingly, at this wavelength the O-atom electronic angular momentum alignment was found to be small, suggesting quenching of the O-atom angular momentum alignment [17]. This contrasts with the behaviour found at shorter wavelengths [23, 24]. Probe-only ion images obtained under a variety of molecular beam stagnation pressures, and corresponding to O-atoms generated in the photodissociation of either the monomer, NO_2, or the dimer, N_2O_4, at 226 nm, were also obtained. In the case of the monomer, for which 226 nm corresponds to excitation into the second absorption band, the kinetic energy release distributions were also found to indicate a strong population inversion in the NO cofragment, and were similar to, though more sharply peaked than, those previously observed in the wavelength range 193 nm to 248 nm [22].

$O_3 + h\nu \rightarrow O_2(a^1\Delta_g/b^1\Sigma_g^+) + O(^1D_2)$:

The singlet channel of the photodissociation dynamics of ozone was investigated at 193 nm [7]. Multiple pump and probe laser polarization geometries and probe transitions were used to enable a comprehensive characterization of the angular momentum polarization of the $O(^1D_2)$ photofragments, in addition to providing high-resolution information about their speed and angular distributions [7]. Images obtained at the probe laser wavelength of around 205 nm indicated that dissociation occurred primarily *via* the Hartley band, involving absorption to, and diabatic dissociation on, the $\tilde{B}^1B_2(3^1A_1)$ potential energy surface. Rather different $O(^1D_2)$ speed and electronic angular momentum spatial distributions were observed at 193 nm, suggesting that the dominant excitation at these photon energies is to a state of different symmetry from that giving rise to the Hartley band, and also indicating the participation of at least one other state in the dissociation process. Evidence for a contribution from absorption into the tail of the Hartley band at 193 nm was also presented. A particularly surprising result was the observation of non-zero, albeit small values for all three rank $K = 1$ orientation moments of the angular momentum distribution. This effect had not previously been observed, and the explanation for these data is far from clear at present. The polarization results obtained at 193 nm and 205 nm, together with those observed previously at longer wavelengths, were interpreted using an analysis of the long range quadrupole-quadrupole interaction between the $O(^1D_2)$ and $O_2(^1\Delta_g)$ species. Subsequent to publication of this work, and partly inspired by it, Schinke and coworkers [15] have performed an extensive set of *ab initio* calculations in the energy region of interest. This investigation corroborates many of the conclusions from our own study, and further demonstrates the value of angular momentum polarization as a valuable tool in helping to determine the mechanism of molecular photodissociation [8, 17].

$O_3 + h\nu \rightarrow O_2(X^3\Sigma_g^-) + O(^3P_J)$:

Speed distributions, and spatial anisotropy and atomic angular momentum polarization parameters were also determined for the $O(^3P_J)$ products following the photodissociation of ozone into the Hartley band at 248 nm and 226 nm [25] (see **Figure 2**). The data were interpreted in terms of two dissociation mechanisms that give rise to fast and slow products. The latter correlate with highly vibrationally excited $O_2(^3\Sigma_g^-)$ products, which have been suggested previously to hold the key to the ozone deficit problem [26]. In both cases, excitation is believed to occur to the $\tilde{B}$ state. Consistent with previous interpretations, the speed distributions, translational anisotropy parameters, and angular momentum polarization moments support the assignment of the major pathway to curve crossing from the $\tilde{B}$ to the repulsive $\tilde{R}$ surface, generating fast fragments in a wide range of vibrational states. For the slow fragments, it was proposed that, following excitation to the $\tilde{B}$ state, the system crosses onto the $\tilde{A}$ state [25]. The crossing seam is only accessible to molecules that are highly vibrationally excited,

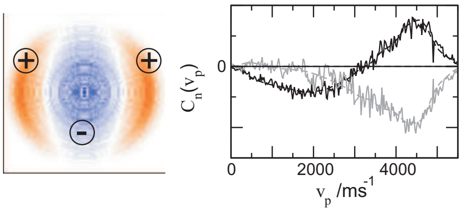

Figure 2: Difference image and Fourier moments for the $O(^3P_2)$ products of the photodissociation of O_3 at 248 nm. The figure illustrates the strong O-atom orientation observed in these experiments [25].

and therefore possess modest recoil speeds. Once on the Ã state, the wavepacket is thought to funnel through a conical intersection to the ground state. The velocity distributions, spatial anisotropy parameters, spin-orbit populations and polarization data each lend support to this mechanism. Although the possibility of the internal conversion pathway has been suggested previously [27], our study provides the first experimental evidence that it is responsible for the production of very highly vibrationally excited O_2 cofragments [25].

$OCS + h\nu \rightarrow CO(X^1\Sigma^+) + S(^1D_2)$:

The dissociation of OCS was investigated subsequent to excitation at 248 nm, with both angular momentum alignment and orientation reported for the channel leading to $S(^1D_2)$. **Figure 3** illustrates the clear dependence of the ion images on the polarization of the probe laser, indicating very strong product angular momentum alignment. In agreement with previous experiments two product speed regimes were identified, correlating with differing degrees of rotational excitation in the CO coproducts [28]. The velocity dependence of the translational anisotropy was also shown to be in agreement with previous work [30, 17]. However, contrary to the accepted interpretation, the speed dependence was shown to reflect primarily the effects of non-axial recoil, and to be consistent with predominant excitation to the $2^1A'$ electronic state. It was proposed that the associated electronic transition moment was polarized in the molecular plane, at an angle greater than ∼60° to the initial linear OCS axis. The atomic angular momentum polarization data were interpreted in terms of the long-range interaction model to help identify likely surfaces populated during dissociation. Although the model neglects coherence between surfaces, the polarization data were found to be consistent with the proposed dissociation mechanisms for the two product speed regimes. Large values for the low and high rank in-plane orientation parameters were also reported. This was believed to be the first example of a polyatomic system for which such effects were found to be of the same order of magnitude as the angular momentum alignment [28].

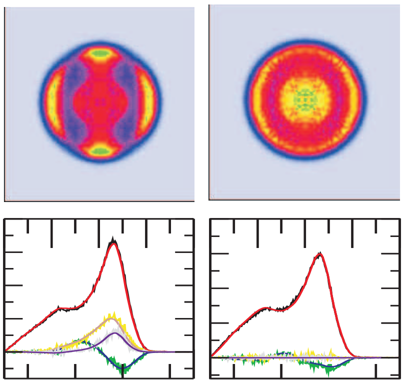
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Figure 3: Images and their Fourier moments for the $S(^1D_2)$ products of the photodissociation of OCS at 248 nm. Left panel: pump and probe linear polarization in the detector plane. Right panel: pump polarization in the plane, probe laser polarization perpendicular to the plane of the detector [28].

$OCS + h\nu \rightarrow CO(X^1\Sigma^+) + S(^3P_J)$:

Speed dependent translational anisotropy parameters, and the atomic angular momentum orientation and alignment, were also measured for the channel leading to $S(^3P_J)$ following excitation at 248 nm [29]. The speed distributions and β parameters were in broad agreement with previous work [30, 17], and show behaviour that is highly sensitive to the S-atom spin-orbit state (see **Figure 4**). The data were found to be consistent with the operation of at least two triplet production mechanisms. Interpretation of the angular momentum polarization data in terms of an adiabatic picture was used to help identify a likely dissociation pathway for the majority of the $S(^3P_J)$ products, which strongly favours production of $J = 2$ fragment atoms, correlated, it was proposed, with rotationally hot, vibrationally cold CO cofragments. For these fragments, optical excitation to the $2^1A'$ surface was thought to constitute the first step in the dissociation process, as for the singlet channel. This is followed by crossing, *via* a conical intersection, to the ground $1^1A'$ state, from which intersystem crossing occurs, populating the $1^3A'/1^3A''(^3\Pi)$ states [29]. The proposed mechanism provided a qualitative rationale for the observed spin-orbit populations, as well as the $S(^3P_J)$ quantum yield and angular momentum polarization. At least one other production mechanism, leading to more statistical S-atom spin-orbit state populations, and rotationally cold, vibrationally hot CO cofragments, is thought to involve direct excitation to either the $^3\Sigma^-$ or $^3\Pi$ states.

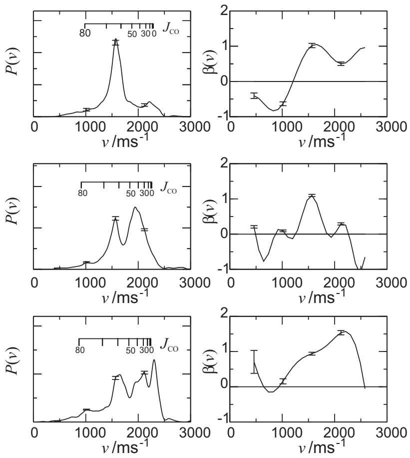

Figure 4: Speed (left) and translational anisotropy (right) distributions for the $S(^3P_J)$ products of the photodissociation of OCS at 248 nm. Top panels: $J = 2$, middle panels: $J = 1$, bottom panel: $J = 0$ [29].

3. Project plan review

Overall, the project proceeded very much as we expected, with experiments conducted, and papers successfully published, on the majority of systems we proposed for study. We still plan to undertake experiments using both tunable pump and probe radiation. In a sense we have been held up by the success of the fixed frequency dissociation studies. These have been more interesting than we thought, and have thus been deserving of a little more time being spent on them.

4. Research Impact

Our research has led so far to publication of ten articles (see the starred papers in the bibliography), nine published in refereed journals, included one Invited 'Cover' article for *Phys. Chem. Chem. Phys.*, and one invited book chapter. The principal beneficiaries of the research were identified in the original proposal as experimentalists and theoreticians working in the field of photochemistry. Our experimental work on N_2O and SO_2 photodissociation led to a very valuable collaboration with Professors O.S. Vasyutinskii (St Petersburg), a world expert on polarization effects in photodissociation, and Professor G.C. Groenenboom (Nijmegen), who developed the fast dissociation model. We have also had close collaborations with Professor F.J. Aoiz in Madrid and Dr M. de Miranda in Leeds on stereodynamical aspects of the project. In addition, we have had fruitful interactions with Professors G.G. Balint-Kurti (Bristol) and R. Schinke (Göttingen), both of whom have a very active interest in many of the systems described. Some of the work on ozone has also involved a collaboration with the groups of Dr G.A.D. Ritchie and Professor G. Hancock in Oxford.

Finally, lists of invited conference presentations and research publications arising from the project are given below.

5. Explanation of expenditure

The expenditure has closely followed that detailed in the original proposal. The Nd:YAG laser has performed extremely well, and we believe was a crucial investment. The project student employed on the grant, Fabio Quadrini, has submitted his D.Phil. thesis and had his *viva voce* examination. He has a very creditable seven publications arising from his thesis work, and his thesis was well received by the examiners. He overlapped partly with a DTA student, Andrew P. Clark, who was also extremely productive, with ten publications from his D.Phil. work. Note that Dr Raluca Cireasa was put on the payroll in June 2004. Although she worked on the project, in particular designing our new ion-imaging chamber, alternative funding was found for her support.

6. Further research and dissemination

Some of the experimental data obtained on this project has yet to be published. As noted above, we also plan to perform new experiments on a number of systems, such as ozone and CS_2. These studies will form the foundation of a future EPSRC proposal.

Invited Conference Presentations: Professor Brouard

1. *October 2005*, Royal Society of Chemistry Symposium, Invited lecture (Leeds, UK).
2. *Sept 2006*, ACS Autumn Meeting, 'Frontiers in Molecular Dynamics', Invited lecture (San Francisco, USA).
3. *July 2006*, Gordon Conference on atomic and molecular collisions, Invited lecture (Colby-Sawyer,USA).
4. *Nov 2006*, Stereodynamics 2006, Invited lecture (Arcachon, France).
5. *Sept 2007*, Gas Kinetics Group Meeting 2007, Invited lecture (Leeds).

Invited Conference Presentations: Dr Vallance

1. ACS Spring Meeting, Anaheim, CA, March 2004, invited talk, 'Imaging molecular photodissociation pathways'
2. CCP6 workshop: Vector correlation and alignment in chemistry, Bristol, July 24-27 2005, invited talk 'Imaging atomic polarization in molecular photodissociation'.
3. Pacifichem 2005, Hawaii, Dec 15-20, 2005, invited talk: 'Product angular momentum polarization in the photodissociation of oxygen'.
4. QuAMP 2007, London, September 10-13, 2007, invited talk: 'Imaging atomic orbital polarization in molecular photodissociation'.

Other members of the group have also spoken or presented posters at numerous national and international conferences, such as Stereodynamics 2006 and the Dynamics of Molecular Collisions (DMC) meeting 2007. Our work has also been presented regularly at departmental seminar presentations.

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