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1. Background

Resonantly enhanced multiphoton ionization (REMPI) coupled with velocity-map ion imaging is an extremely powerful tool for probing the dynamics of elementary photochemical processes [1]. It provides a high resolution projection of the speed and angular distribution of the recoiling products, in principle at the product quantum state level. However, it is only very recently that velocity-map ion imaging techniques have been applied to bimolecular collisional processes. Such studies fall into two classes, those which attempt to study collisional processes under crossed molecular beam conditions [2, 3, 4, 5], and those which combine REMPI ion imaging detection with the photon-initiated reaction technique [6, 7]. The latter method employs a coexpansion of the atomic or radical photolytic precursor together with the target molecular reactant in a single molecular beam. This affords higher reactant number densities, and hence sensitivity, than the crossed-molecular beam method. The study of photon initiated reactions, using what is commonly referred to as the *photoloc* method [8], is a particular speciality of the Oxford group [9], and the principal objective of the original proposal was to build a velocity-map ion imaging machine capable of being applied to the study of elementary photon-initiated bimolecular reactions.

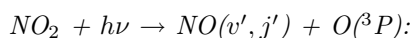
2. Key advances

Technical achievements:

We have successfully constructed and tested a new velocity-map ion imaging apparatus, shown schematically in Figure 1. A pulsed molecular beam is crossed orthogonally by polarized photolysis and probe laser radiation. Photofragments or reaction products are detected quantum state selectively after a short time imaging delay using REMPI coupled with velocity-map [10] ion imaging [11]. The latter technique involves ‘pancaking’ the expanding ion cloud onto a position sensitive, multichannel plate (MCP) detector. Ion impact at the MCPs generates a cascade of electrons which are then accelerated onto a phosphor screen, and observed using a CCD camera.

A further important development has centred around 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 [12], which can be applied to a distribution without cylindrical symmetry (such as those observed when the photofragments are polarized, as illustrated below). An alternative, powerful solution to the inversion problem is that of slice imaging [13], an experimental technique that directly generates a slice through the full 3D velocity distribution. However, in spite of this elegant experimental solution to the problem, there has been considerable interest in the inversion procedure developed in Oxford, particularly by those performing experiments in situations where slice imaging may not be practicable. Of more importance to us, the method is very well suited to the analysis of ion images arising from the products of photon-initiated bimolecular reactions.

The experiments described below illustrate the capabilities of the apparatus we have constructed, and highlight some of the specific achievements of the research undertaken over the last three years.



One of the first systems studied on the new apparatus was the photodissociation of NO_2 at 308 nm. Although this molecule is a benchmark system for study, comparatively little work has been performed at energies significantly above the dissociation threshold (i.e. at $\lambda \ll 400$ nm). However, we had previously undertaken a comprehensive study of orientation and alignment effects in the NO products of the photofragmentation of room temperature

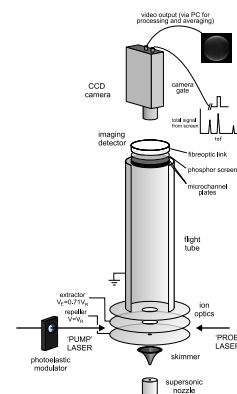


Figure 1: Schematic of the velocity-map ion imaging apparatus.

NO₂ at 308 nm using laser induced fluorescence (LIF) detection [14]. This system, therefore, provided a sensible starting point, to assess both our ion imaging apparatus, and our analysis procedures. A comparison of the vector quantities determined under the two conditions is shown in Table 1, expressed in terms of bipolar moments [15], together with the raw ion images from which they were obtained (see Figure 2). The agreement between the two

$k_2 = 0$		$k_2 = 2$			
$\beta_0^0(00)$	$\beta_0^2(20)$	$\beta_0^2(02)$	$\beta_0^0(22)$	$\beta_0^2(22)$	$\beta_0^2(42)$
1.00	0.61 (2)	-0.23 (2)	-0.38 (2)	0.27 (4)	-0.27 (5)
1.00	0.70 (5)	-0.36 (2)	-0.50 (11)	0.30 (7)	-0.08 (6)

Table 1: Bipolar moments obtained for the NO($v' = 0, N' = 29$) photofragments subsequent to the photodissociation of NO₂ at 308 nm. Top row: Room temperature LIF experiments; bottom row: jet-cooled velocity-map ion imaging results [12].

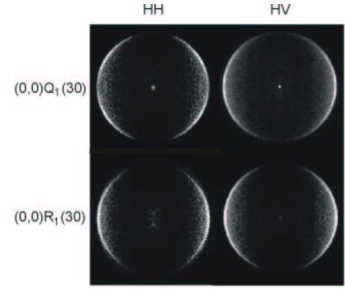
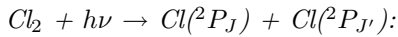


Figure 2: NO images obtained subsequent to 308 nm photodissociation of NO₂ [12].

sets of data is remarkably good. Notice that the ion imaging experiments tend to yield bipolar moments of larger magnitudes than the LIF measurements. This result is fully consistent with the colder rotational temperature of NO₂ generated under jet-cooled expansion conditions, which reduces the ‘blurring’ of the vector properties induced by parent molecular rotation.



Due to the depolarizing effects of nuclear spin, the determination of the electronic orbital polarization of the Cl(²P_{3/2}) atomic fragments of Cl₂ photodissociation provides a particularly sensitive test of the ion imaging apparatus [16]. We have performed a study of the photodissociation of Cl₂ at 308 nm, a wavelength at which detailed polarization measurements had not been performed previously. The ion images obtained are shown in Figure 3. The effect of orbital angular momentum polarization is particularly noticeable as a difference between the images for the VH pump-probe geometry (i.e. photolysis and probe linear polarization vectors respectively perpendicular with, and parallel to, the image plane) when the probe transition is changed from a Q[↑] (upper panel) to P[↑] (lower panel) transition. The data were used to help provide insight into the electronic states accessed during dissociation, and in particular about the role of non-adiabatic effects in molecular chlorine photodissociation [17].

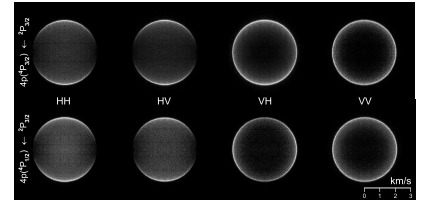
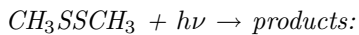
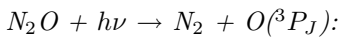


Figure 3: The dependence of velocity-map ion images of Cl(²P_{3/2}) atoms, generated in the photodissociation of Cl₂ at 308 nm, on pump-probe geometry and probe transition [17].



The versatility of our photofragment ion imaging machine is illustrated further by our recent study of the photodissociation and dissociative ionization pathways in dimethyl disulphide. This molecule is an important sulphur precursor in the atmosphere, and its 193 nm induced photodissociation had previously been studied by conventional time-of-flight mass spectrometry [18]. The use of velocity-map ion imaging provides high speed and angular resolution, and has revealed a complex array of competing dissociative and ionization processes [19], hitherto only partially characterized.



One of the most exciting and unexpected results to come out of our ion imaging studies has been our study of the photodissociation of N₂O. It was our intention to use N₂O photodissociation as a clean source of O(¹D₂) atoms for the study of electronic quenching. Although this might still be possible, it proved difficult because of background O(³P_J) atoms directly generated by photolysis of N₂O. The process, of course, is spin-forbidden, with a quantum yield of less than 3% [20], and the observation of O(³P_J) in our experiments provides some measure of the sensitivity of our apparatus. Of more interest is the fact that ground state oxygen atoms are born with *polarized* total electronic angular momentum, which is opposite in sign for $J = 1$ or $J = 2$ [21].

Analysis of this result [21] suggests that the polarization of the total electronic angular momentum, $\mathbf{J}' = \mathbf{L}' + \mathbf{S}'$, where \mathbf{S}' is the total electron spin, reflects the polarization of the electronic *orbital* angular momentum, \mathbf{L}' . Electron spin appears to play the role of a spectator, as expected in the fast recoil limit [21]. In this limit, the *orbital* alignment ($M_{L'}$ sub-level populations) can be determined from measured $M_{J'}$ populations, and used to generate a map of the O-atom unpaired electron density (see adjacent figure). The electron density distribution is found to lie preferentially perpendicular to the recoil direction (\mathbf{v}), consistent with the two unpaired electrons occupying *p*-orbitals with $m_{l_1} = +1$ and $m_{l_2} = -1$, and proving *unambiguously* that dissociation occurs on a surface with ${}^3\Sigma^-({}^3A'')$ symmetry in the asymptotic region. This state is most likely populated through spin-orbit coupling with the singlet surface responsible for (spin-allowed) dissociation into $\text{O}({}^1D_2) + \text{N}_2$ products [21]. However, other pathways are possible (such as direct photon absorption to a triplet state), and future measurements of alignment and orientation as a function of photodissociation wavelength, together with further theoretical work, should help to distinguish these alternative mechanisms. This future work, together with polarization studies of other photodissociation systems forms the basis of a new project recently funded by EPSRC (see below).

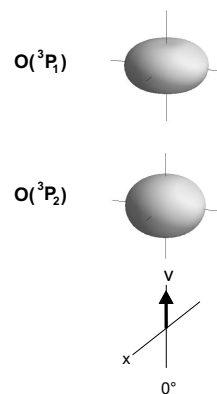


Figure 4: Unpaired electron density distribution in the $\text{O}({}^3P_J)$ fragments of N_2O photodissociation [21].

We have also performed preliminary experiments on the photodissociation of SO_2 . The resulting ion images reveal that the $\text{O}({}^3P_J)$ products are also orbitally aligned [22]. Although a full analysis is yet to be completed, the results suggest, interestingly [23], that dissociation occurs preferentially on the ground electronic potential energy surface, following internal conversion from the $\tilde{\text{C}}$ state.



The study of reactive bimolecular collisional processes using velocity-map ion imaging is particularly demanding because of the low number of products probed in the small REMPI interaction volume. To help develop our apparatus in Oxford we collaborated, in an E.U.-funded project at the FORTH Institute, with the Crete group of T.N. Kitsopoulos, who have led the way in applying ion imaging methods to the study of photon-initiated reactions [5, 6]. However, the exchange also provided an opportunity for us to test the data analysis procedures we have developed specifically for the study of such reactions [9, 12]. In these experiments, the Cl atom reactants were generated by pulsed laser photolysis of Cl_2 at 355 nm. The $\text{HCl}(v' = 0, j')$ reaction products of the H-atom abstraction reaction between Cl and ethane were probed quantum state selectively using the (2+1) REMPI transitions around 240 nm [7].

Velocity-map ion-images were obtained for $\text{HCl}(v' = 0)$ rotational levels $j' = 0$ to 6. The angular distributions were observed to shift from forward scattering to backward scattering with increasing HCl angular momentum, confirming the general trends in angular scattering distribution observed in the pioneering REMPI core extraction experiments by the Zare group in Stanford [24]. However, the quality of the ion-images, combined with the use of the aforementioned analysis procedures, also allowed us to extract quantum state-resolved fractional kinetic energy release distributions, $P(f_t)$. As a consequence of energy conservation, these provide information about the internal excitation in the ethyl radical coproduct [7]. Interestingly, the results suggest that on average about 20% of the available energy is deposited in ethyl fragment internal excitation. This degree of excitation is consistent with the ethyl radical rotational excitation that would be generated by impulsive release of the small barrier energy in the exit channel. Note that, while the transition state of the reaction is linear in the Cl-H-C₂H₅ coordinate (consistent with the absence of significant rotational excitation in the probed HCl product), it is non-linear in the H-C-C coordinate. The derived angular scattering and kinetic energy release distributions, combined with the $\text{HCl}(v' = 0, j')$ rotational population distributions determined by Zare and coworkers [24], can be used to generate a velocity-angle contour map of the reaction, which is shown in Figure 5. The plot is compared with the results of a previous crossed molecular beam study of the Cl plus propane reaction by Suits and coworkers [25]. The similarities in the two sets of data are striking, and support our finding that the ethyl cofragments of the reaction don't behave as spectators to

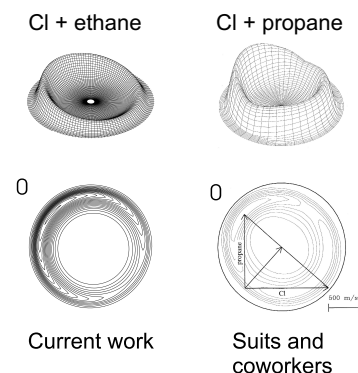


Figure 5: Comparison of the velocity-angle polar plots of angular distributions obtained for Cl + ethane [7], and previously by Suits *et al.* for Cl + propane [25].

reaction. Our conclusions are further supported by a new wave of parallel beam ion imaging experiments being developed by the Crete group [5].

A parallel set of experiments were performed on the Cl atom reaction with butane [26]. The general trends in scattering distribution with $\text{HCl}(v' = 0)$ rotational state are similar to those described above for the simpler Cl atom reaction with ethane. They are also in reasonable accord with very recent parallel beam experiments from the Crete group [5]. The new feature in the experiments described here is the ability to distinguish the relative efficiencies of H atom abstraction at primary versus secondary sites. This is made possible because the two pathways possess different energetics. The shift from predominantly primary attack (and forward scattering) to secondary attack (and more backward scattering) with increasing HCl rotational angular momentum is broadly consistent with the HCl/DCl rotational population measurements of Dagdigian and coworkers following reaction of Cl with partially deuterated propane [27].



We have recently obtained our first results on a bimolecular reaction system using our machine in Oxford, with a study of the Cl atom reaction with methane [28]. In these experiments, the CH_3 products were probed on the (2+1) REMPI transitions around 330 nm. The relatively high sensitivity of the apparatus may be gauged from the low cross-section for this reaction, compared with that for Cl plus ethane, coupled with the inefficiency of the CH_3 REMPI transitions, compared with those in the HCl.

A typical velocity-map ion image is shown in Figure 7. We have analyzed this image assuming no internal excitation of the HCl and methyl products, in agreement with previous experiments [29]. A consistent fit to the data can only be achieved if a contribution is allowed from reaction of vibrationally excited methane (either in the torsional, ν_2 , or bending, ν_4 , mode), which is inefficiently cooled in the jet expansion. The resulting differential cross-sections for ground and vibrationally excited methane are shown in Figure 8. We find about $38 \pm 6\%$ of the CH_3 products are generated from reaction with vibrationally excited methane, which is in reasonable agreement with a previous estimate from the group of Zare obtained under similar experimental conditions [29].

There has been considerable debate about the role of bending and/or torsional modes in promoting the Cl plus methane reaction [29, 30]. In an attempt to unravel which of these modes might be responsible for the enhancement in the present experiments we have recently completed a further set of experiments on the deuterated reactions $\text{Cl} + \text{CD}_4$ and $\text{Cl} + \text{CH}_3\text{D}$. The availability of two reactive channels in the latter system make it particularly interesting, and it has recently been the subject of bond-selective chemistry experiments by the group of Crim and coworkers [31]. Figure 9 shows a REMPI scan of the CH_3 and CH_2D radical products in the region of the $\text{Q}\uparrow$ branch of 0_0^0 vibronic bands. The relative yields of the two products are approximately in the statistical ratios for abstraction of an H or a D atom. However, in the light of the fact that a significant amount of reaction comes from vibrationally excited CH_3D , a statistical interpretation of the product ratio might not be appropriate. Analysis of the CH_3 and CH_2D ion images should help clarify this point.

3. Project plan review

Overall the project has proceeded as we had expected. Some of the work has taken longer than we had anticipated, but I believe this has been compensated for by our unexpectedly interesting results on alignment effects in the photodissociation of N_2O . It should also be mentioned that we were held up for four months earlier this

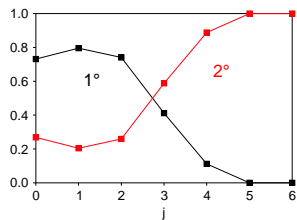


Figure 6: Branching ratio for Cl abstraction of primary versus secondary H atoms in the reaction Cl plus butane.

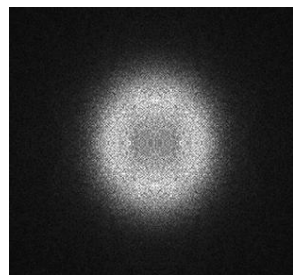


Figure 7: Ion image of the CH_3 products of the Cl + methane reaction.

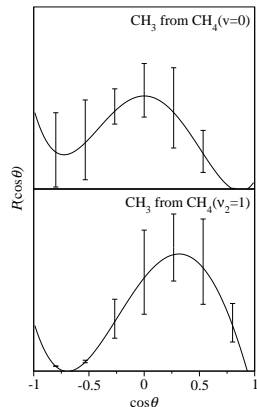


Figure 8: Angular scattering distributions for the Cl + CH_4 reaction with ground and vibrationally excited methane [28].

year due to the failure of our MCP detector, which took much longer than we had hoped to repair. This in particular delayed our progress on bimolecular reaction studies. In spite of this hold-up, we have successfully proved the basic analytical and experimental methodology, one of the main goals of our proposal, and believe that there are now many systems (including the specific systems identified in the original proposal) that are potentially amenable to study.

4. Research Impact

The principal beneficiaries of the research were identified in the original proposal as experimentalists and theoreticians working in the field of reaction dynamics. As already noted, our work on Fourier moment analysis of ion images [12] has received considerable attention in the ion imaging community. Our experimental work on N_2O photodissociation led to a very beneficial collaboration with Professor O.S. Vasylutinskii (St Petersburg), a world expert on polarization effects in photodissociation, and his theoretical input on this project has been invaluable [21]. We have developed further interactions with the group of Professor G.C. Groenenboom (Nijmegen) and both him and Professor Vasylutinskii will be valuable collaborators on our new EPSRC-funded project (see below) [22]. Our studies on the Cl plus ethane and butane reactions performed in Crete in collaboration with Professor T.N. Kitsopoulos [7, 26] are already being used as a benchmark by which other techniques [5] are being assessed. It should also be mentioned that the development of the ion-imaging experiments in Oxford also led to a collaborative project with the group of Professor B. Martínez Haya, from Seville, funded by the Royal Society [17, 19]. Finally, lists of invited conference presentations and research publications arising from the project are given below.

5. Explanation of expenditure

The expenditure closely followed that detailed in the original proposal. The project student employed on the grant, Mark Bass, is likely to submit his D.Phil. thesis in the next few months.

6. Further research and dissemination

Much of the experimental data obtained on this project has still to be published, and this of course is our immediate objective. However, the apparatus developed here has opened up the possibility of several new studies. Our proposed research on electronic orbital angular momentum polarization has recently received support from EPSRC (GR/S69313/01). Our studies of bimolecular collisions form the basis of a recently submitted proposal for a new EU Research Training Network on reaction dynamics of complex systems. Much of the work described here has of course already been presented at the annual meetings of our current EU Network.

Invited Conference Presentations

1. 27th International Symposium on Free Radicals, July 2004, (Taipei, Taiwan).
2. Royal Society of Chemistry Symposium, February 2003, (University College, London).
3. Stereodynamics of Chemical Reactions 2002, December 2002, (Schoorl, Holland)
4. MOLEC XIV, September 2002 (Istanbul, Turkey).
5. IBER 2002, March 2002 (Lisbon, Portugal).
6. XIX International Symposium on Molecular Beams, June 2001, (University of Rome).
7. Stereodynamics 2000, December 2000, (El Escorial, Spain).

The following lectures (2-4 of which were invited) have also been presented by Dr Claire Vallance:

1. High Resolution Spectroscopy and Gas Kinetics Discussion group meeting, December 2001, (Birmingham, UK).
2. XVIII International Conference on Molecular Energy Transfer, June 2003, (El Escorial, Spain).
3. Symposium on Atomic, Cluster and Surface Physics, February 2004, (La Thuile, Italy).
4. 227th ACS National meeting, March 2004, (Anaheim, CA, USA).

Other members of the group have also spoken or presented posters at numerous national and international conferences, such as COMET 2003. Our work has also been presented annually at our EU Research Training Network meetings, and departmental seminar presentations.

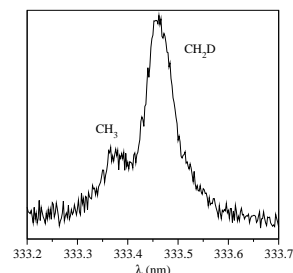


Figure 9: REMPLI scan of the CH_3 and CH_2D products of the $\text{Cl} + \text{CH}_3\text{D}$ reaction.

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References in bold face arise from work carried out on this proposal.

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