

M. Brouard**1. Background**

The object our research was to study rotational angular momentum polarization effects in the products simple elementary chemical reactions. Although the rotational polarization in the products of bimolecular reactions had been predicted to provide valuable information about the (stereo-)dynamics of elementary reactions, principally through the pioneering work of Herschbach and coworkers [1], two factors made the proposed research particularly timely. Firstly, it was only around the mid-to-late nineties that the methods for calculating angular momentum polarization were fully developed. The applicant was directly involved in developing quasi-classical trajectory (QCT) methods to study polarization in bimolecular reactions [2, 3], while the quantum mechanical (QM) formalism was developed particularly by Clary and de Miranda and their coworkers [4]. Since that time, several important papers have reported on QM and QCT stereodynamical calculations for the $\text{H} + \text{D}_2$ [5], $\text{O}(^1\text{D}) + \text{H}_2$ [6, 7], $\text{Li} + \text{HF}$ [8] and $\text{H} + \text{H}_2\text{O}$ [4]. These calculations all pointed to the rich dynamical behaviour that measurements of angular momentum polarization should potentially expose. The QCT studies, in particular, have highlighted the necessity of determining both angular momentum *orientation* and *alignment* if a complete stereodynamical picture is emerge. At the time, angular momentum orientation, or *planar chirality* as it has been coined [9], had not been observed in any bimolecular collision or molecular photodissociation process.

A second factor which made the research timely was the parallel development of experimental methods which allowed rotational polarization effects to be reliably determined [2, 10]. Our own work [2] provided a means of extracting *scattering angle dependent* orientation and alignment information from the Doppler-resolved laser induced fluorescence spectra of nascent reaction products. It built upon earlier studies from our own group [11], as well as upon key developments from the group of Zare and coworkers [12, 13]. Since the start of the research programme there has been increased interest in measuring angular momentum polarization effects in a variety of collisional and photon-initiated processes, including several measurements of angular momentum orientation effects, primarily in molecular photodissociation [14, 15, 16, 17, 18]. Although much of the latter work has focused on measuring electronic orbital angular momentum orientation in atomic photofragments, *rotational* angular momentum orientation effects have also received attention [14, 19, 20], including work from our own group described below [21]. In an important recent development, Cline and Chandler and coworkers have now observed planar chirality in the inelastic scattering of NO by Ar [22].

The study of polarization effects in chemical reactions is very much a ‘hot topic’ in the field of reaction dynamics. Our own achievements and contributions to the field, which have arisen through the support of the EPSRC grant, are summarized below. Much of this material has been discussed in recent major reviews written by other researchers in the field [23, 24, 25, 26].

2. Key advances

Technical achievements: The major experimental achievements centred on improving the sensitivity of our laser pump-probe experiments to rotational polarization effects, principally by using photoelastic modulators to switch pump and/or probe laser polarizations on alternate laser shots. In addition, we have developed a method for detecting the planar chirality of the products generated by linearly polarized photodissociation or bimolecular reaction. Such measurements require determining certain non-zero *odd* orientation moments of the correlated angular momentum distribution, and this is made possible using circularly polarized probe radiation, coupled with detection of *elliptically* polarized emitted radiation in the 1+1 laser induced fluorescence (LIF) sequence. Needless to say, the inclusion of polarizing optics in the detection system places rather heavier than usual demands on the detection sensitivity. We believe our measurements on NO_2 photodissociation, described further below, were the first to determine all photofragment rotational polarization moments up to and including those of order (rank) 3.

The above experiments are also supported by interface and data analysis software. One key step has been developing a code to determine the sensitivity of the experiments to polarization moments in any arbitrarily chosen pump-probe-detector geometry. Although the necessary linestrength theory was in the literature [28], putting theory into practice proved a non-trivial task. The completed code is an invaluable aid in planning polarization measurements.

$\text{O}(^1\text{D}_2) + \text{H}_2 \rightarrow \text{OH}(v', j') + \text{H}$: The reaction of $\text{O}(^1\text{D})$ with H_2 has been the focus of much previous work, both by our own group [29] and by others [26]. A particular interest has been in establishing at what collision energies excited electronic states start to play a significant role. There are a total of five potential energy surfaces (PESs)

which correlate with the $O(^1D_2 + H_2)$ reactants, of which the lowest three are believed to be the most important. Reaction on the ground $1^1A'$ PES proceeds *via* insertion of oxygen into H_2 , producing a short lived, vibrationally excited HOH intermediate. By contrast, reaction on the first excited $1^1A''$ PES proceeds *via* a direct abstraction mechanism, similar to that in operation in the $F + H_2$ reaction. A third $2^1A'$ electronic state correlates with electronically *excited* OH products, and can only lead to reaction *via* non-adiabatic coupling to the ground state: calculations suggest its role is likely to be minor at collision energies around 0.1 eV [30].

Our experiments were designed to address two key issues: does the $1^1A''$ PES participate in the reaction at collision energies around 0.12 eV (just above the calculated barrier on that PES), and which of the different versions of the PESs involved most reliably describes the reaction dynamics. We focused on rotational quantum-state population and high precision rotational alignment measurements on the OH products born in high vibrational levels $v' = 2, 3, 4$, since reaction on the excited A'' PES was predicted to lead to a vibrational population inversion, rather like in the $F + H_2$ reaction. Our work benefited enormously from collaborations with the theoretical groups of Aoiz (Madrid) and Launay (Rennes), who were able to provide the first state-to-state QM scattering calculations on the reaction. Our key findings are summarized in figure 1 below.

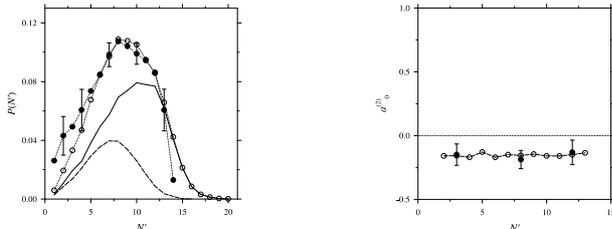


Figure 1 The OH($v' = 4$) rotational population distribution (left) and rotational angular momentum alignment (right) (where $a_0^2 \equiv \langle P_2(\hat{\mathbf{k}} \cdot \hat{\mathbf{j}}) \rangle$, the second Legendre moment of the \mathbf{k} - \mathbf{j} distribution) for the $O(^1D) + H_2$ reaction. Filled circles - experimental results, open circles - QM scattering theory including contributions from the $1^1A''$ excited state. The continuous and dashed lines in the left figure are the calculated contributions from the ground $1^1A'$ and excited $1^1A''$ state PESs [31].

The population and alignment data suggest convincingly [31] that the Dobbyn-Knowles [32] versions of the $1^1A'$ and $1^1A''$ PESs are the most reliable surfaces available: an earlier version of the excited state PES by Schatz and coworkers [33] performs significantly less well in comparison with the experiments. More interestingly, the experimental data pointed unequivocally in favour of a contribution from reaction on the excited state surface [31]: its participation has the effect of cooling the OH($v' = 4$) rotational distribution, and makes the rotational alignment parameters more negative, consistent with the involvement of a direct reaction on the excited state surface. Finally, we were able to demonstrate that near quantitative agreement between experiment and theory can only be achieved using QM scattering methods: the QCT calculations although qualitatively correct were unable to account quantitatively for the OH rotational population distributions [31, 34].

$H + H_2O/D_2O \rightarrow OH/OD(v', j') + H_2/HD$: This important four-atom reaction has been the subject of detailed experimental study by our group over a number of years. We have determined OH quantum-state populations, rotational alignment parameters, differential cross-sections, and kinetic energy release distributions for the H atom reactions with both H_2O and D_2O at two collision energies. We have also measured the reaction cross-section for the $H + H_2O$ at 2.5 eV. Given this large amount of material [35], it is perhaps not surprising that theoreticians have found it difficult to reproduce all aspects of our experimental data.

In the light of the experiments of Crim [36], Zare [37], and Smith [38] and their coworkers on the H atom reaction with vibrationally excited water, there is general consensus that the OH moiety behaves like a spectator to reaction. However, until recently, theoretical calculations using QCT methods consistently over-estimated the degree of excitation in the OH products [39]. At a collision energy of 1.4 eV we have shown that the OH population data can be modeled beautifully using a Franck-Condon model, in which OH product rotation originates solely from zero-point bending and rotational motion in the parent HOH molecule. The model also accounts for the strong lambda-doublet propensities observed in the reaction. Two newly developed PESs, one from Schatz and coworkers [40], and the other from Zhang and Collins [25, 41], now yield much better agreement with experimental OH populations. We have also measured, with high precision, the rotational angular momentum alignment in the OH products: consistent with the above spectator picture, the alignment at 1.4 eV is near zero. More interestingly, the alignment remains small at higher collision energies, where the Frank-Condon ‘spectator’ model clearly breaks down. In contrast to early predictions, QCT calculations employing some of the most recent PESs reproduce this near-zero OH alignment.

One particularly interesting feature is the kinetic energy release distribution in the OH products, which, by energy and momentum conservation, provides information on the *internal* energy disposal in the H_2/HD coproducts. We have found that the H_2/HD energy disposal changes significantly between the collision energies of 1.4 eV and

2.5 eV. At high energies, our data for HD are fully consistent with the direct measurements of the HD populations by Zare and coworkers [37], which indicate significant HD rovibrational excitation, as one might expect for the newly forming HD species. By contrast, at the lower collision energy the amount of H₂/HD internal excitation observed in our experiments is very small, with around 80% of the available energy released into product translation. Although the qualitative trend of increasing internal H₂/HD excitation with increasing collision energy is reproduced in a number of QCT studies, the latter have generally failed to provide quantitative agreement with experiment. It would appear that until recently the global PESs available have not been sufficiently accurate in the exit channel region. Furthermore, there is some evidence that quantum mechanical effects (such as zero point energy constraints) might have an important influence on the H₂ energy disposal. QCT calculations [25] on the very latest Zhang and Collins PES [41] are shown in figure 2, where they are compared with experiment, and with similar calculations on an earlier PES by Clary and Ochoa [42]. The newer QCT calculations yield much improved energy disposal data in comparison with experiment: QM scattering calculations on the same PES appear to yield even better agreement, although at the moment these calculations are approximate, and have only been performed for $J = 0$ [43].

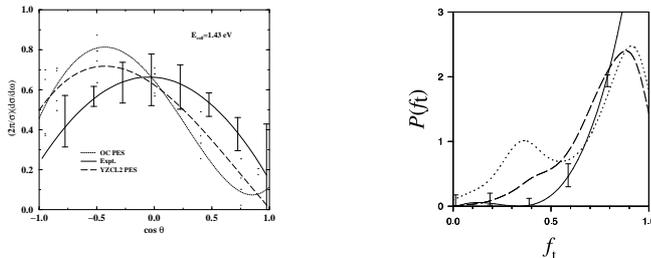


Figure 2 The differential cross-section and kinetic energy release distribution for the OH($^2\Pi_{1/2}, v' = 0, j' = 0$) fragments of the H + H₂O reaction at 1.4 eV. The experimental data (smooth lines with error bars) are compared with QCT calculations [25, 39] on recent PESs by Clary and Ochoa (dotted line) [42] and by Zhang and Collins (dashed line) [41].

Another important discrepancy between theory and experiment, which emerged during the project as a result of the QM scattering calculations of Zhang and Collins [41], concerns the absolute cross-sections for the abstraction reaction. This had been measured previously, most notably by Wolfrum’s group [44], and was typically between a factor of ten to twenty times larger than those predicted by theory over a range of collision energies. We have employed a different calibration procedure to that used in the original experiments by Wolfrum and coworkers [44], and obtain a much smaller abstraction reaction cross-section [35], which is in better agreement with theory [41]. The OH population distribution, which is derived from the same measurements, also agrees very well with QCT theory on the new Zhang-Collins PES [25]. At present, however, the origin of the discrepancy between our experiments and those reported previously is unclear.

$H + N_2O/CO_2 \rightarrow OH(v', j') + N_2/CO$: These isoelectronic H atom reactions both possess deep potential energy wells corresponding to formation of HNNO and HOCO intermediates. However, the reaction with N₂O is also predicted to undergo a direct abstraction reaction following attack of the H atom at the terminal O-atom end of the target molecule [45]. Contrary to theoretical prediction [45], measurements of the OH quantum state resolved differential cross-sections suggest that complex formation is probably the dominant pathway for both systems [46]. The angular distributions are highly sensitive to OH rotational quantum state, changing from forward-backward peaking at low N' , to sideways peaking at high N' . At present we do not have a *quantitative* explanation for this behaviour, although again it is common to both systems.

Measurement of the OH quantum-state resolved kinetic energy release distributions for the H + N₂O reaction are particularly revealing [46]. They show that about 50% of the available energy is released into the internal modes of the N₂ cofragment. The energy release data is remarkably similar to that found in the photodissociation of N₂O [47] and HN₃ [48] *via* their first excited electronic states, both of which are known to generate highly rotationally excited N₂ fragments. We proposed [46] that the similarity in dynamical behaviour arises because the response of the target molecules to the incoming H atom in the bimolecular reaction mirrors that of the target molecule (or other isoelectronic molecules) to photon excitation. The model is similar to that employed by Herschbach and coworkers to rationalize the dynamics of the three-atom H + Cl₂ reaction [49].

Despite the fact that both reactions proceed *via* short-lived intermediates, rotational polarization effects were found to be quite large, especially in the case of the H atom reaction with N₂O [50] - see figure 3(a). The survival of angular momentum polarization partly reflects angular momentum conservation constraints: a significant fraction of the product rotational angular momentum originates from orbital angular momentum of the reactants, which is necessarily directed perpendicular to the reactant relative velocity vector, \mathbf{k} . However, the product rotational angular momentum polarization also reflects forces operating in the exit channel of the reaction, and this polarization is not scrambled on formation of a rotating collision complex. The polarization observed in the

full collision under these conditions is analogous to the $\mathbf{v}\text{-}\mathbf{j}$ correlation observed in molecular photodissociation.

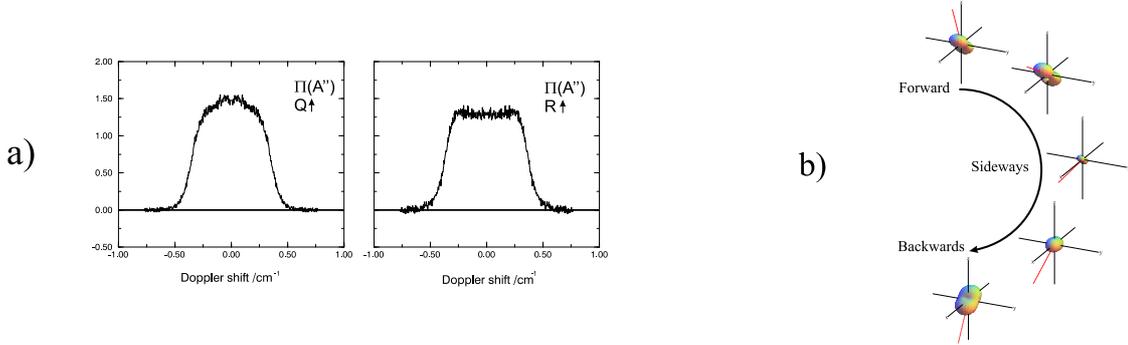
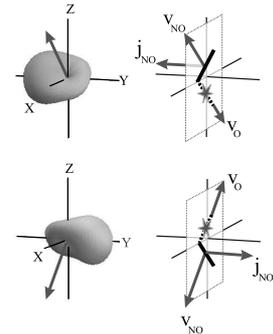


Figure 3 (a) Raw Doppler resolved profiles for $Q\uparrow$ and $R\uparrow$ transitions probing the A'' lambda-doublet level of $\text{OH}(v' = 0, N' = 5)$ generated in the $\text{H} + \text{N}_2\text{O}$ reaction at a collision energy of 1.5 eV. The difference in line-shape arises *exclusively* from the effects of rotational polarization. (The corresponding A' lambda-doublet level is unpolarized within experimental error.) (b) Polar plot of the $\text{OH}(v' = 0, N' = 5, A'')$ rotational angular momentum alignment as a function of CM scattering angle. The bold line represents the direction of product recoil and lies in the zx scattering plane. Note that the angular momentum (the alignment of the ‘lobe’ in the polar plot) tends to point along the recoil direction [50].

Analysis of the polarization data for the $\text{H} + \text{N}_2\text{O}$ reaction reveals a surprising result [50]. OH products are born with a preference for their rotational angular momentum vectors to lie *parallel* to the product relative velocity vector \mathbf{k}' (the direction of OH recoil) - see figure 3(b). Qualitatively similar behaviour is observed in the isoelectronic $\text{H} + \text{CO}_2$ reaction [51]. The data suggest that dissociation of the HNNO (HOCO) complex occurs with significant out-of-plane torsional excitation. Remarkably, the photodissociation of HN_3 *also* generates $\text{NH}(^1\Delta)$ products with $\mathbf{v} \parallel \mathbf{j}$, consistent with the dominance of torsional forces in the exit channel [48]. Once more, the dynamics of the H atom reaction with N_2O bears striking similarities with the photodissociation of the ‘electron poor’ HN_3 species.

$\text{NO}_2 + h\nu \rightarrow \text{NO}(v', j') + \text{O}(^3P)$: A parallel set of experiments were performed to characterize the rotational angular momentum polarization in the NO products of the 308 nm photodissociation NO_2 . The measurements were partly motivated by the ion imaging experiments by Cline and coworkers [14], but were also designed to verify our detection and data analysis procedures. However, we believe the results proved rather more interesting than anticipated [21]. There were two technical aspects to the experiments which we initially wanted to address. Firstly, we wished to demonstrate that it is possible to extract a complete set of polarization moments from a *single* probe transition, thus avoiding the necessity of recording data on both $Q\uparrow$ and $P/R\uparrow$ branch transitions (which usually requires the use of weak satellite lines). Secondly, we hoped to demonstrate the use of Doppler-resolved LIF methods to determine both angular momentum orientation *and* alignment information. As noted above, we believe our experiments were the first to measure *all* moments of the angular momentum distribution up to and including rank 3.

Figure 4 *Left panels*: the rotational angular momentum polarization of the $\text{NO}(v' = 0, N' = 29)$ photofragments of the 308 nm photodissociation of NO_2 . Note that in the upper left panel the angular momentum points preferentially along the $-y$ axis whereas it lies along the $+y$ axis in the lower panels [21]. *Right panels*: Cartoons of the dissociation mechanism. In all figures the bold arrow represents the direction of NO recoil. Note that the planar symmetry of molecular photodissociation or bimolecular reaction dictates that the products can only be oriented along the y axis.



As with the $\text{H} + \text{N}_2\text{O}$ reaction, the polarization information is most conveniently represented in the form of a polar plot [21], showing the (semiclassical) probability of \mathbf{j}' lying in a particular direction: the bold vectors in the left panels of figure 4 show the direction of NO recoil (cf. figure 3(b)). The cartoons on the right show the mechanism of NO_2 dissociation. The orientation measurements suggest that dissociation occurs with concomitant bond angle closing. This might be associated with impulsive energy release in the breaking bond. However, the sense of the orientation might also reflect reductions in bond angle associated with photon excitation, and subsequent passage through a conical intersection with the ground state: the latter must be traversed if dissociation is to occur [52]. A key point is that the angular momentum orientation provides completely new dynamical information that is not contained in the alignment moments alone.

In further work [53] we have determined angular momentum orientation and alignment parameters for a range of $\text{NO}(v' = 1, N')$ fragments born in different rotational states. While the rotational alignment parameters increase monotonically with rotational quantum number N' , the first orientation moment, $\beta_0^2(21)$ in the notation of Dixon [27], passes through a maximum. The origin of the behaviour is not fully understood yet, but it suggests a subtle change in the predominance of bond-angle closing and opening mechanisms with NO rotational state. Again, such information could not be derived from alignment measurements alone.

$\text{H} + \text{O}_2 \rightarrow \text{OH}(v', j') + \text{O}$: Our first attempts at measuring angular momentum orientation in a bimolecular reaction involved probing the OH products of the $\text{H} + \text{O}_2$ reaction at 2.5 eV. Although the reaction involves formation of a short-lived HO_2 complex, Doppler-resolved experiments by G.E. Hall and coworkers [54] revealed strong rotational angular momentum alignment, and highly *asymmetric*, forward-peaking differential cross-sections (suggesting a very short lifetime for any HO_2 complex formed). On the strength of these results, we measured the OH orientation in this system, but found it to be zero within our experimental error. The dynamical measurements by Hall and coworkers [54] suggest that the OH orientation is not scrambled by HO_2 complex rotation: we believe that our null result is probably associated with the rapid exchange of H between the two equivalent O atoms in the transitory HO_2 complex, which would also serve to smear-out any rotational orientation.

$\text{O} + \text{HBr}/\text{HCl} \rightarrow \text{OH}(v', j') + \text{Br}/\text{Cl}$: Finally, we have performed preliminary studies of the stereodynamics of the $\text{O}(^3\text{P}) + \text{HBr}$ and HCl reactions [55]. Our intention here is to look at a direct three-atom reaction, which is likely to possess strong angular momentum orientation. We have recently shown that the rotational alignment of the OH products of the O atom reaction with HBr is significant, indicating a strong preference for $\mathbf{j}' \perp \mathbf{k}$, despite the light atom transfer kinematics [55]. In addition to rotational alignment data, we have also determined the $\text{OH}(v' = 1, N' = 5)$ differential cross-section. This displays preferential forward scattering, consistent with the kinematics of the reaction. OH Doppler profile measurements have also revealed that the kinetic energy release for $\text{OH}(v' = 1, N' = 5)$ products is consistent with the Br coproducts being generated in both ground and excited spin-orbit states with near equal reaction probabilities [55]. The data support earlier conclusions drawn by Zare and McKendrick and coworkers based on a surprisal analysis of the $\text{OH}(v' = 1)$ rotational distributions [56].

Preliminary experiments on the $\text{O} + \text{HCl}$ system have been performed in which fast $\text{O}(^3\text{P})$ has been produced through photolysis of NO_2 at 248 nm and 193 nm. Although the latter wavelength is also sufficiently energetic to generate $\text{O}(^1\text{D})$, the excited atoms react almost exclusively with HCl to generate vibrationally excited OH products. Our $\text{OH}(v' = 0)$ Doppler profile measurements appear to confirm this picture, and are inconsistent with OH production from the $\text{O}(^1\text{D}) + \text{HCl}$ reaction. In addition, Doppler profiles recorded using circularly polarized probe radiation reveal the OH products to be rotationally oriented. If this proves correct, once the data are fully analyzed, it will represent the first determination of planar chirality in a bimolecular reaction.

3. Project plan review

Although progress has been more rapid on some systems than others, overall the project has proceeded very much as outlined in the plan of the original proposal.

4. Research Impact

Of the studies described above, we would highlight our work on the $\text{O}(^1\text{D}) + \text{H}_2$ and $\text{H} + \text{H}_2\text{O}$ reactions, and the photodissociation of NO_2 as being of particular impact and benefit to others in the field. As noted above, our data on the $\text{H} + \text{H}_2\text{O}$ reaction has been very widely used to test current *ab initio* and dynamical theory, and much of our work has been discussed in detail in a number of recent reviews [23, 24, 25, 26]. In addition, our studies have led to five invitations to present talks at major international meetings (as listed at the end of this report). I have also been invited to write a feature article on the research described here for the Journal of Physical Chemistry A, which has recently been submitted for publication.

5. Explanation of expenditure

The expenditure closely followed that detailed in the original proposal. The major cost was for staff: the post-doctoral researchers employed on the grant made very significant contributions to the project. The first left after 14 months to take up a post-doctoral position with Dr D. Rowley (UCL) in atmospheric chemistry, an area which was closer to her long-term interests. The second RA is now an EU-funded post-doctoral assistant in Paris. The project student employed on the grant submitted his D.Phil. thesis in a little over three years, and is due to be examined at the end of November 2001.

6. Further research and dissemination

Much experimental data is still to be published, particularly on the $\text{H} + \text{H}_2\text{O}$ reaction, for which we await the results from our theoretician collaborators before proceeding into press. As noted above, our future experiments will focus on confirming angular momentum orientation in the $\text{O} + \text{HCl}$ and $\text{O} + \text{HBr}$ reactions. We also plan

orientation measurements on the OH products generated by the H + H₂O reaction: these experiments would have been attempted sooner had it not been for the fact that it became apparent during the project that the reaction cross-section for this system is even smaller than originally believed at the collision energies accessible to us (see above).

Partly on the strength of the research described here, the group is now a member of an EU Network on *Reaction Dynamics*, which comprises both experimental and theoretical groups. There is growing interest in measuring angular momentum orientation and alignment both in the products of bimolecular reactions, and in molecular photodissociation. Experiments of this type are still very much in their infancy: we believe that we (and others) have demonstrated their potential as valuable tools for elucidating reaction mechanism.

Invited Conference Presentations

1. XIX International Symposium on Molecular Beams, June 2001, (University of Rome)
2. Stereodynamics 2000, December 2000, (El Escorial, Spain)
3. 16th International Gas Kinetics Symposium, July 2000, (Cambridge University)
4. Royal Society of Chemistry Symposium, May 2000, (Oxford University)
5. MOLEC Conference, September 1998, (University of Bristol)

Our research has also been presented by members of the group at numerous national and international meetings, including the Free Radicals meeting in Assisi, 2001, and the MOLEC meeting in Jerusalem, 2000.

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