

Summary of Research

The Stereochemistry of Chemical Reactions

Grant GR/K66758

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Chemically reactive collisions are dramatic events, involving a wholesale reorganisation of the reagents' atomic and molecular structure, as they evolve into the scattered reaction products. The direct observation of such events is no easy task. Until recently, their dynamics were most often probed by using a mass spectrometer to monitor the angular distributions of products scattered from the collision of two crossed molecular beams. Unfortunately, this approach is generally blind to much of the dynamical detail, since the mass spectrometer cannot distinguish between products scattered into different quantum states. A new approach, developed independently by the investigators at Oxford and by Professor Richard Zare's group at Stanford, has transformed the situation. A pulsed laser is used to initiate reaction, which can now be studied in a bulb, and the mass spectrometer is replaced by a delayed pulse of tunable, polarised, narrow line laser radiation to allow Doppler-resolved, quantum state selection, *optical* detection of the scattered products. The spatial distributions of both their velocities and rotational angular momenta can be revealed through analysis of their Doppler line-shapes to provide a uniquely detailed, three-dimensional view of the *stereo*-dynamics of *individual* reactive collisions.

At the outset of the research programme, the technique was still in its infancy. Only a handful of reactions had been explored and little was understood about the quantitative analysis of rotational angular momentum distributions, let alone their interpretation. Over the period of the programme, we have refined the experimental and analytical techniques, established the new strategy to the point where it has effectively superseded the pioneering, crossed molecular-beam method, and applied it to an array of chemical reactions which are of great importance in atmospheric and combustion chemistry. These include the reactions of excited, O(¹D) atoms (generated in the upper atmosphere *via* the photolysis of ozone) with methane, hydrogen (and its isotopes) and hydrogen chloride; and the reaction of atomic hydrogen with carbon dioxide, nitrous oxide and water. In almost every example, the results have led, or are leading, to re-evaluations of the present understanding of the reactive collision dynamics. They have also catalysed new theoretical and computational programmes that can (hopefully) better model the new, quantum state-resolved experimental results - particularly the spatial, *vectorial* distributions of the scattered reaction products. The synergism between theory and experiment is particularly intense since the new experiments are now leading theory: as one of the best international theoreticians in the United States recently wrote, 'the experiments that you and Mark are doing have provided much to challenge the poor theoreticians'. They can be expected to continue to do so for some years to come.

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1. Background

The original research proposal was conceived at a time when the study of the stereodynamics of bimolecular reactions using photon-initiated (or *photoloc* [1]) methods, coupled with Doppler-resolved spectroscopic probing of the reaction products [2], was still in its infancy. Only a handful of systems had been explored, data acquisition and analysis strategies were in a primitive state of development, and little was understood about the quantitative analysis of rotational polarization effects, let alone their interpretation. In the following we show how this picture has been changed during the period of the research grant, and in section 3, highlight some of the ways in which our recent experiments have provided “detailed insight and understanding” of the stereodynamics of elementary chemical reactions. We describe some of the new directions in which these studies are being developed in section 4.

2. Technical achievements and developments

The technical advances we have made are perhaps best illustrated by reference to some recently acquired experimental data for the H + CO₂ reaction (see below) [3]. Figure 1 shows Doppler-resolved *composite* line-profiles for OH($v' = 0, N' = 1$), obtained at a centre-of-mass (CM) collision energy of 2.5 eV. The composite profiles were generated by forming linear combinations of Doppler profiles obtained on different rotational branches and in alternative pump-probe laser configurations, a procedure which projects out terms in the full Doppler profile dependent on the laboratory (LAB) speed (figure (a)) distribution and the LAB translational anisotropy (figure (b)) [2]. The experiments were performed at a total pressure of 100 mTorr, with a time delay of 80 ns, ample to ensure single collision conditions, yet allowing excellent signal-to-noise ratios to be achieved. Indeed the quality of the data is so good that the raw speed dependent data is obscured by the fit to it, shown as a solid black line in figure (a). The figures, together with the resulting angular scattering distributions and kinetic energy release distributions to be discussed in section 3(d), also demonstrate the improvements made in the data fitting and error analysis procedures: the latter, in particular, allows for kinematic and energetic constraints which influence the CM speed and angular resolution of the experiment.

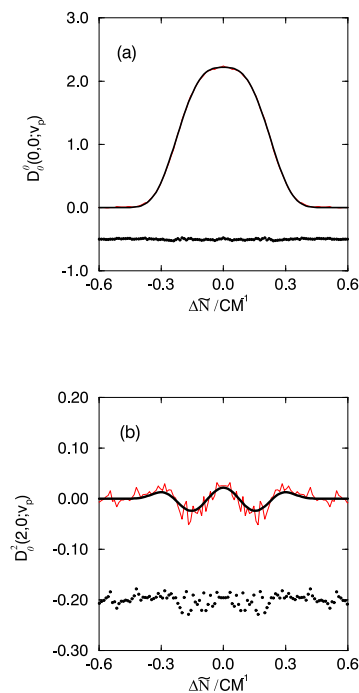


Figure 1

Perhaps some of the most significant advances have been made in developing quantitative methods for experimentally determining CM product rotational polarization information [4], and for the simulation of such properties by quasi-classical trajectory (QCT) methods [5]. Both aspects of the research have benefited enormously from a collaboration with the group of Professor F.J. Aoiz in

the Department of Chemistry, Complutense University, Madrid. Some of the new experimental results will be discussed in section 4. One particular feature to emerge from the theoretical work has been the importance of product rotational *orientation* (in addition to rotational *alignment*) as a diagnostic of reaction mechanism: this aspect of the research is now being funded through EPSRC grant GR/L97339.

3. Reaction Stereochemistry

(a) $\text{O}(^1\text{D}) + \text{CH}_4 \rightarrow \text{OH}(v', j') + \text{CH}_3$

Our study of the insertion reaction of $\text{O}(^1\text{D})$ with CH_4 was the first to provide quantitative product state-resolved angular scattering and kinetic energy release distributions, as well as angular momentum polarization information [6, 7, 8]. Reactive channels leading to $\text{OH}(^2\Pi_{3/2}, v' = 0, N' = 5, 8)$ in both A' and A'' Λ -doublet levels, and $\text{OH}(^2\Pi_{3/2}, v' = 4, N' = 8)$ were probed. Products born in $v' = 4$ were found to be scattered with near forward-backward symmetry, as would be consistent with the generation of a *rotating* CH_3OH^* complex. In contrast, products generated in $v' = 0$ were found to be scattered preferentially in the backward hemisphere. This behaviour was ascribed to a dependence of the state-resolved opacity functions on the scattered OH vibrational level. It was proposed that low impact parameter collisions lead preferentially to OH products with low vibrational excitation. These products are generated *via* dissociation of collision complexes which possess low rotational angular momenta and, therefore, long rotational periods. The angular scattering in these low $\text{OH}(v')$ channels is therefore characteristic of *short-lived* (non-rotating) collision complex. The OH products born in $v' = 4$ are generated by much higher impact parameter collisions, which lead to production of *rotating* collision complexes, and scattering angular distributions displaying characteristic forward-backward symmetry. Such a scenario was also shown to be consistent with the measured OH state-specific kinetic energy release distributions, which could be modeled using statistical phase-space theory, *provided* the $v' = 4$ products were assumed to be generated from high orbital angular momentum collisions.

(b) $\text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH}(v', j') + \text{H}_2$

In a parallel experimental and (QCT) theoretical study [9, 10, 11, 12, 13], our attention turned to the simplest $\text{O}(^1\text{D})$ insertion reactions with H_2 , HD and D_2 . QCT calculations [9, 10] on a modified version of an early potential energy surface (PES) by Schinke and Lester [14] predicted dramatic variations in angular scattering distributions with OH rovibrational state, reminiscent of the behaviour found experimentally for the $\text{O}(^1\text{D}) + \text{CH}_4$ reaction described above. Our early experiments focused on measuring the angular scattering distributions for the $\text{OH}(v' = 0)$ products born in low ($N' = 5$) and intermediate ($N' = 14$) rotational levels (shown as the dashed curves in figure 2(a) and (b)). The angular distributions were found to be in good qualitative accord with QCT calculations employing the Schinke-Lester PES (see figure 2, bold curves), and more recently with QCT calculations employing the newer, more accurate PESs of Schatz and Harding [15], and

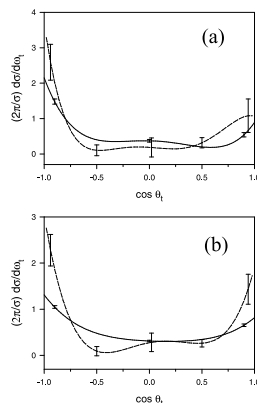


Figure 2

of Dobbyn and Knowles [16] (this latter surface was developed as part of the EPSRC funded HPCI consortium).

Concurrently with our own work, the experimental groups of Liu [17], Casavecchia [18] and Suits [19] were also studying the same systems using a variety of methods, all of which, however, lacked the resolution to observe scattering into individual OH quantum states. These studies provided new evidence that, with increasing collision energy, the global (OH state-averaged) angular scattering distributions become more backward scattered, behaviour which was ascribed to an increased rôle of reaction on excited electronic PESs. These findings were supported, at the time, by QCT calculations on the excited $1^1A''$ PES of Schatz and Harding [15], and by surface hopping calculations between the ground $1^1A'$ and excited $2^1A'$ surfaces derived from the diatomic in molecules method [21].

The need to invoke reaction on excited state PESs at elevated collision energies is not in itself surprising. The important issue, particularly in relation to the calculation of the reaction rate constant at elevated temperatures, is the range of collision energies over which reaction can be satisfactorily described in terms of motion over the *ground state* PES alone. Stimulated in particular by the earlier of the theoretical predictions [20], we embarked on a study of the $\text{OH}(v' = 4, N' = 1)$ products of the reaction [13]. Even at the relatively low collision energies sampled in our experiments, reaction to generate low rotational states of $\text{OH}(v' = 4)$ was predicted to be *dominated* by reaction on the excited $1^1A''$ PES [20, 13]. However, the experimental angular scattering distributions showed no sign of strong backward scattering [13], the signature of reaction over the $1^1A''$ excite state potential [20]. We note that the latest QCT calculations [22] on the most recent and accurate PESs of Dobbyn and Knowles [16] predict significantly smaller rôles for both the $1^1A''$ and $2^1A'$ states at the collision energies sampled in our experiments. A more definitive understanding of the involvement of excited electronic states in the simplest $\text{O}(^1\text{D})$ insertion reaction must await further experiment, and, in the longer term, quantum scattering calculations [23, 24] on at least three coupled potential energy surfaces.

(c) $\text{O}(^1\text{D}) + \text{HCl} \rightarrow \text{OH}(v', j') + \text{Cl}$

Our study of the $\text{O}(^1\text{D})$ reaction with HCl [25] preceded the above investigations of the reaction with H_2 . Although kinematically more friendly than reaction with the lighter partner, the study was made more demanding because of competing reactions of $\text{H} + \text{N}_2\text{O}$ yielding $\text{OH}(\text{X}) + \text{N}_2$ and $\text{OH}(\text{A}) + \text{N}_2$. The former competing reaction (discussed in more detail below) leads to production of $\text{OH}(v' \leq 2)$. Since the insertion reaction with HCl leads preferentially to population of higher OH vibrational levels [26], this complication is not a severe one. The second competing reaction of $\text{H} + \text{N}_2\text{O}$, generating electronically excited OH radicals, proved more problematic because it meant that the $\text{OH}(\text{A} \leftarrow \text{X})$ LIF spectra, of necessity, had to be measured against a background spontaneous emission from $\text{OH}(\text{A})$.

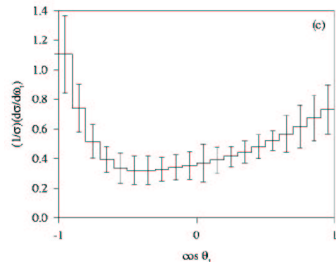


Figure 3

In spite of these difficulties we were able to obtain the differential cross-section for the OH($v' = 4, N' = 6$) products of the reaction at a mean collision energy of ~ 0.5 eV (see figure 3). The scattering was found to be broadly distributed, but showed a distinct peak in the backward hemisphere. The angular distribution was found to be qualitatively similar to the global (state-averaged) angular distribution observed by Casavecchia and coworkers [27] for the competing reaction leading to ClO products. Scattering into both chemical channels was interpreted (by both groups) in terms of competing abstraction versus insertion mechanisms (the latter accounting for the broad forward-backward symmetric component of the angular distribution). However, in the light of our subsequent study of the O(1D) + H₂ reaction, it is conceivable that a mechanism involving production of short-lived HOCl (HClO) collision complexes might also account for the observations.

(d) $\text{H} + \text{CO}_2 \rightarrow \text{OH}(v', j') + \text{CO}$

The reaction of translationally hot H atoms with CO₂ has been a favourite of experimentalists and theoreticians in recent years. Although reaction is believed to proceed *via* the HOCO intermediate, there are uncertainties about its lifetime [28, 29], and its participation at elevated collision energies is unclear. Our first experiments [30, 3] revealed dramatic changes in differential cross-section with both quantum state and collision energy. Some representative data are shown in figure 4. Figures (a) and (b) are the angle-velocity contour plots for OH fragments born in $v' = 0, N' = 1$ at mean collision energies of 1.8 and 2.5 eV. Figure (c) shows an analogous contour plot for the OH($v' = 0, N' = 5$) products generated at 2.5 eV. We first interpreted the the low collision energy data in terms of production of a *short-lived* HOCO collision complex, with changes in the differential cross-section with collision energy reflecting a move to more direct scattering dynamics. However, after an exhaustive set of experiments, it now transpires that the stereodynamics of the reaction is even more subtle, and depends on the OH spin-orbit state, at least at low N' , where the OH $^2\Pi$ radical approaches the Hund's case a coupling scheme. The data shown in figures 4(a) and (b), which display anisotropic scattering more akin to a direct reaction, were both obtained on the lowest rotational state of the upper spin-orbit level, $^2\Pi_{1/2}$. Our most recent experiments on the lowest rotational levels of the $^2\Pi_{3/2}$ state show much more isotropic (and forward-backward symmetric) scattering, as do products born in higher rotational levels, where OH approaches a Hund's case b coupling limit. At present our angular scattering data are consistent with production of OH $^2\Pi_{3/2}$ radicals *via* a rotating collision complex. The same mechanism also accounts for the $^2\Pi_{1/2}$ OH products generated in high rotational levels. Production of low rotational levels of OH $^2\Pi_{1/2}$, on the other hand, appears to take place *via* a more direct mechanism, possibly involving an excited electronic potential energy surface. This work is to be submitted as a very full paper in the near future [31].

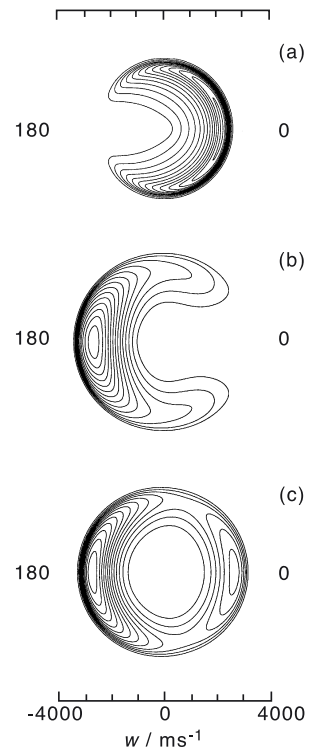


Figure 4



Although the $\text{H} + \text{N}_2\text{O}$ system is isoelectronic with $\text{H} + \text{CO}_2$, and analogous to the HOCO intermediate possesses a local minimum in the potential energy surface at configurations corresponding to HNNO, the two systems have very different energetics and the stereodynamics of the $\text{H} + \text{N}_2\text{O}$ reaction are dominated by the huge energy release in the exit channel. The possibility of (distinguishable) H atom attack at either end of the NNO molecule adds a further dimension of dynamical interest. We have determined angular scattering distributions and kinetic release distributions for seven OH quantum states at a mean collision energy of 1.5 eV [32, 33]. The angular scattering distributions are characteristic of those produced by dissociation of a rotating collision complex, but change from forward-backward peaking to sideways peaking as the OH rotational excitation is increased. This behaviour has yet to be explained quantitatively. Unlike the HOCO system, no evidence for a dependence of the scattering distributions on OH spin-orbit state has been observed.

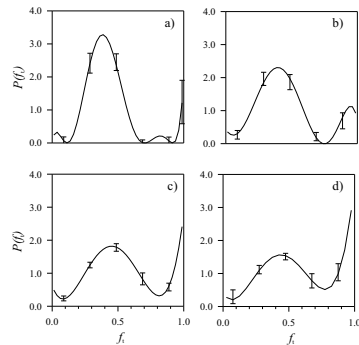
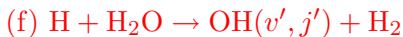


Figure 5

Figure 5 shows the kinetic energy release distributions for four of the OH quantum states investigated ($v' = 0, N' = 5$ figure (a), $v' = 0, N' = 9$ (b), $v' = 0, N' = 14$ (c), and $v' = 1, N' = 6$ (d)). As the OH internal excitation increases we find increasing bimodal structure in the kinetic energy release distributions, which we associate with the operation of competing *microscopic* mechanisms [33]. The dominant mechanism involves HNNO complex formation, subsequent to H atom attack at the terminal N atom of NNO, and is responsible for the products born with low kinetic energy release (high N_2 internal excitation). The highly repulsive exit channel, which is accessed after H atom migration to the O atom, is believed to bear many similarities with the first excited electronic states of the (pseudo-isoelectronic) molecules N_2O and HN_3 [32]. Both excited states can be accessed by photon absorption, and are known to generate highly rotating N_2 products, characterized by kinetic energy release distributions very similar to those shown in figure 5. The second microscopic mechanism is believed to be direct, and involve H atom abstraction of the terminal O atom in ONN: this mechanism is associated with internally cold N_2 products and hotter than average OH products. At present the experimental data are very poorly modeled by QCT simulation [34].



Finally, we have undertaken a detailed study of one of the simplest four-atom systems, $\text{H} + \text{H}_2\text{O}$ [35]. We have determined differential cross-sections and kinetic energy release distributions for OH born in three quantum states, and have recently extended the work to a number of OD channels in the H atom reaction with D_2O . As shown in figure 6 the scattering for $\text{OH}(v' = 0, N' = 1)$ products is predominantly in the sideways direction, a result which at first seems surprising given the rebound dynamics observed by Casavecchia and coworkers [36] for the

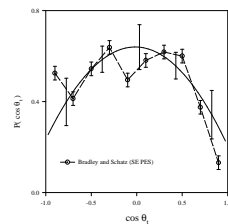


Figure 6

reverse reaction of OH with D₂. The results have been interpreted in terms of the opening in the cone of acceptance as the collision energy is raised [35], a result which seems to be born out by QCT calculations on a recently developed potential energy surface [37] (see open points on figure 6). Interestingly, full dimensionality quantum scattering calculations [38] on an older PES account for the experimental kinetic energy release distributions (see figure 7), even though QCT calculations on that surface fail to reproduce the observed angular scattering distributions. It would appear that a PES of sufficient accuracy (both in the transition state region *and* in the exit channel)

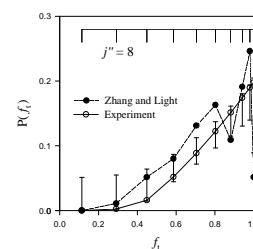


Figure 7

to account fully for all the experimental findings is currently not available. We note finally that the scattering dynamics appears acutely sensitive to isotopic mass. Under the same conditions as were employed to obtain the angular scattering shown in figure 6, the H atom reaction with D₂O leads to strong scattering in the backward hemisphere. This behaviour probably arises because of the lowering of the reactant and, to a lesser extent, transition state zero-point energies but a quantitative explanation must await detailed QCT or QM calculations.

4. Future directions

We close with an example of the determination of rotational polarization effects in an elementary chemical reaction, which in our view points the way to future studies of dynamical stereochemistry. In figure 8, experimentally derived polar plots are displayed which show snap-shots of the OH($v' = 0, N' = 5$) rotational angular momentum polarization for the H + N₂O at two CM scattering angles (in these figures the reagents approach along the z-axis and the products are scattered along the red-dashed vector). The figures show that at both scattering angles (corresponding to scattering in the backward (upper figure) and forward (lower figure) hemispheres) the OH rotational angular momentum vector prefers to lie *along* the direction of product recoil. The data suggest that OH rotation must arise preferentially from *torsional* forces in the transition state. Similar behaviour has been observed in the OH products of the H + CO₂ reaction. Note that to date much of the theoretical work on both of these systems has focused on the *planar* HNNO and HOCO intermediate complexes. Our new data suggest very forcibly that *non-planar* configurations are important, particularly in the exit channel of these reactions.

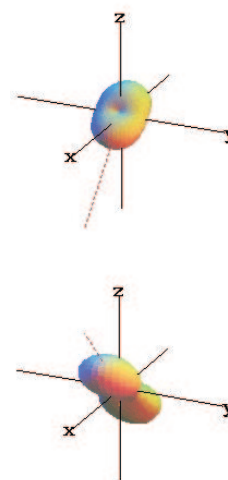


Figure 8

5. References

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13(i) Publications arising from the EPSRC grant

1. "A quasi-classical trajectory study of the reaction $O(^1D) + HD \rightarrow OH(D) + D(H)$." A J Alexander, F J Aoiz, M Brouard and J P Simons; *Chem. Phys. Lett.* **256**, (1996), 561
2. "Product state-resolved stereodynamics: $O(^1D) + HCl \rightarrow OH + Cl$." A J Alexander, M Brouard, S P Rayner and J P Simons ; *Chem. Phys.* **207**, (1996), 215.
3. "Product state-resolved stereodynamics of the reaction $H + CO_2 \rightarrow OH + CO$." M Brouard, H M Lambert, S P Rayner and J P Simons; *Mol. Phys.* **89**, (1996), 403
4. "Product rotational polarization in photon-initiated bimolecular reactions." F J Aoiz, M Brouard and P A Enriquez; *J. Chem. Phys.* **105**, (1996), 4964
5. "An experimental and quasi-classical trajectory study of the product state resolved stereodynamics of the reaction: $O(^1D) + H_2 \rightarrow OH(X^2\Pi; v' = 0, N' = 5) + H$." A J Alexander, F J Aoiz, M Brouard, I Burak, Y Fujimura, J Short and J P Simons; *Chem. Phys. Lett.* **262**, (1996), 589
6. "Product rotational polarization: The stereodynamics of the $F + H_2$ reaction." F J Aoiz, M Brouard, V J Herrero, V Saez Rabanos and K Stark; *Chem. Phys. Lett.* **264**, (1997), 487
7. "Stereodynamics of the reaction $O(^1D_2) + H_2 \rightarrow OH(v' = 0, N', f') + H$: state-resolved Linear and rotational angular momentum distributions." A J Alexander, F J Aoiz, L Banares, M Brouard, J Short and J P Simons; *J. Phys. Chem.*, **101**, (1997), 7544.
8. "Classical reaction probabilities, cross-sections and rate constants for the $O(^1D_2) + H_2 \rightarrow OH + H$ reaction." A J Alexander, F J Aoiz, L Banares, M Brouard, V J Herrero and J P Simons; *Chem. Phys. Lett.*, **278**, (1997), 313.
9. "The $H + H_2O \rightarrow OH + H_2$ reaction: OH state-resolved differential cross-sections and H_2 co-product internal energy disposals." M Brouard, I. Burak, G A J Markillie, K E W M^cGrath and C. Vallance; *Chem. Phys. Lett.*, **281**, (1997), 97.
10. "The state resolved stereodynamics of the insertion reaction $O(^1D) + H_2 \rightarrow OH(v', N') + H$." A J Alexander, F J Aoiz, M Brouard, J Short and J P Simons; *Israel J. Chem.* **37** (1997) 317.
11. "Product state-resolved dynamics of the reaction $H + N_2O \rightarrow OH + N_2$." M Brouard, I Burak, S Gatenby and G A J Markillie; *Chem. Phys. Lett.*, **287**, (1998), 682.
12. " $O(^1D_2) + H_2 \rightarrow OH(v', N', f') + H$: the anatomy of a reaction." A J Alexander, D A Blunt, M Brouard, J P Simons, F J Aoiz, L Banares, Y Fujimura and M Tsubouchi; *Faraday Discuss. Chem. Soc.* **108** (1997) 375.
13. "Chemistry with a sense of direction: the stereodynamics of bimolecular reactions." A J Alexander, M Brouard, K S Kalogerakis and J P Simons; *Chem. Soc. Rev.*, **27** (1998) 405.

14. "An experimental study of the dynamics of the reaction $\text{H} + \text{CO}_2 \rightarrow \text{OH} + \text{CO}$: Product state-resolved differential cross-sections and translational energy release distributions."
M Brouard, D W Hughes, K S Kalogerakis and J P Simons; *J. Phys. Chem.*, **102** (1998) 9559.
15. "The $\text{H} + \text{N}_2\text{O} \rightarrow \text{OH} + \text{N}_2$ reaction at 1.5 eV: New evidence for two microscopic mechanisms."
M Brouard, I. Burak, S.D. Gatenby, D. Hart and D. Minayev; *J. Chem. Phys.* in press.
16. "OH spin-orbit state dependent dynamics of the $\text{H} + \text{CO}_2 \rightarrow \text{OH} + \text{CO}$ reaction."
M Brouard, K S Kalogerakis, D W Hughes and J P Simons; In preparation.

13(ii) Invited Talks, Seminars and Lectures Series

1. Faraday Discussion **113**, *Stereochemistry and Control in Molecular Reaction Dynamics*
Leeds, July 1999, Spiers Memorial Lecture (JPS)
2. COMET Conference, *Invited Lecture*
Assisi, June 1999 (JPS)
3. Faraday Discussion **108**, *Dynamics of Electronically Excited States in Gaseous, Clusters and Condensed Media*
Sussex Dec 1998, Invited paper (JPS)
4. *George C Pimentel Memorial Lecture*
UC Berkeley, February 1998 (JPS)
5. *Invited Seminar*
Univ Paul Sabatier, Toulouse, March 1998 (JPS)
6. *Invited Seminar*
Univ of Pittsburgh, January 1998 (JPS)
7. 9th European Workshop, *Photon Induced Dynamics*
Toulouse, November 1997, Invited paper (presented by D Blunt)
8. Conference on *Dynamics of Molecular Collisions*
Minnesota, July 1997, *Invited lecture* (JPS)
9. Conference on *Stereodynamics of Chemical Reactions*
Bielefeld, December 1996, *Invited lecture* (JPS)
10. 14th International Gas Kinetics Symposium, *Michael Polanyi Lecture*
Leeds, September 1996 (JPS)
11. *Erskine Lecture Series*
University of Canterbury NZ, February-March 1996 (JPS)
12. MOLEC Conference, *Invited Lecture*
Bristol, Summer 1998 (MB)
13. American Chemical Society Summer Meeting, *Orientation and alignment in chemical reactions*
San Francisco, USA, *Invited Lecture*, Summer 1997 (MB)
14. American Chemical Society Summer Meeting, *Bimolecular Interactions of Small Free Radicals*
Orlando, USA, *Invited Lecture*, 1996 Summer (MB)
15. OSA International Quantum Electronics Conference, *Laser spectroscopy and Dynamics*
Sydney, Australia, *Invited Lecture*, Summer 1996 (MB)
16. Faraday Discussion **102**, *Unimolecular Reaction Dynamics*
Oxford University, December 1995, *Invited Paper* (MB)