Report on Research: Grant GR/H09393

The research programme has been directed along two major interconnected avenues: the characterization of rovibrationally highly excited molecules using the double-resonance technique of vibrationally mediated photodissociation, and the exploitation of polarized laser pump-probe techniques to study the full-collision stereodynamics of photon-initiated bimolecular reactions at the product state selective level.

Quantum state resolved photodissociation dynamics of H_2O and HOD

The photodissociation dynamics of water *via* its first excited state is one of the most studied and perhaps best understood polyatomic photodissociation processes. Of most relevance in the present context is the half-collision dynamics initiated from fully reagent rotational and vibrational quantum state selected H_2O, studied experimentally by Andresen *et al.* [1], Crim and Coworkers [2] and Rosenwaks and Coworkers [3], and theoretically using quantum dynamics calculations, most notably of Schinke and Coworkers [4]. Prior to the present studies, the general consensus was that provided the photon energy is below the $H + OH \rightarrow HO + H$ barrier on the $\tilde{A}$ state surface, product OH rovibrational state distributions primarily reflect the rovibrational character of the selected initial $H_2O(\tilde{X})$ state and are little influenced by exit channel effects on the excited state surface. Hence, long wavelength photodissociation of water initially prepared with $J = 0$ in 'zero order' local mode states of the form $|n0^{\pm}0\rangle$ [1] leads to rovibrationally cold OH fragments, photolysis from selected states $|nm^{\pm}0\rangle$ generates enhanced yields of vibrationally excited products, and fragmentation from initial states with additional quanta in the bending mode and/or higher levels of parent rotational excitation gives rise to more rotationally excited product molecules. The success of a one-dimensional (1D) Franck-Condon model developed by Balint-Kurti [5] in reproducing the OH rotational distributions (including Λ-doublet and spin-orbit populations) observed in many of these experiments lends considerable support to the notion that exit channel effects play a minor role in determining the product state distributions.

The key purpose of the study undertaken was to exploit this intimate link

[1] The $|nm^{\pm}k\rangle$ label refers to the symmetric (+) or antisymmetric (-) local mode state with n quanta in one OH stretch, m in the other OH stretch and k quanta in the bend.

between selected reagent state and the photofragment quantum state populations to explore the variation in the rotational-bending motion of $H_2O(\tilde{X})$ as a function of H—OH bond separation. This was achieved by dissociating rotationally state selected water molecules prepared in the $|40^-0\rangle$, $|50^-0\rangle$ and $|40^-2\rangle$ vibrational levels *via* excitation into the (state-specific) $\tilde{A} \leftarrow \tilde{X}$ absorption continua at $\lambda \simeq$ 282 nm [6]. Energy conservation, together with the Franck-Condon principle, requires preferential excitation from a region close to the outer maximum of the intermediate state wavefunction [2], and thus the photofragment state distributions should reflect the rotational-bending motion of the water molecule at extended values of the H—OH bond length, R. In addition, selection of alternative initial states and photolysis wavelengths allows control of the range of R values over which the intermediate state is sampled in the photodissociation process.

The important findings from the study are summarized as follows:

i Photodissociation of parent molecules with $J = 0$ generates $OH(^2\Pi)$ rotational state distributions, and Λ-doublet and spin-orbit populations, which are relatively insensitive to dissociation wavelength and initial OH stretching vibrational excitation. The result is consistent with the 1D Franck-Condon model [6] (employing the modified Sorbie-Murrell potential [7] to calculate the bound state bending-rotational wavefunction at fixed bond lengths), which predicts little variation in photofragment state distributions as the H—OH bond length, R, is increased. This surprising behaviour arises because of an accidental balancing of decreasing bending vibrational force constant and increasing (H—OH) moment of inertia as R is increased and is a specific attribute of the bound state water potential [6].

ii Dissociation of parent molecules with $J > 0$, in contrast, leads to photofragment rotational and fine structure state distributions which *are* sensitive to both the parent vibrational state and the photolysis wavelength. The same Franck-Condon model referred to above accounts qualitatively for the observations provided long wavelength dissociation from high lying OH stretching states of water is assumed to occur preferentially at extended values of R.

[2] The $\tilde{A}$ state of water is dissociative and correlates with the same ground state fragments as the $\tilde{X}$ state.

The calculations also establish that the observed variations in OH state distributions primarily reflect changes in the inertial properties of water as R increases (note that the water molecule becomes more prolate top as R$\rightarrow \infty$) [6]. More detailed comparison between theory and experiment reveals that the values of R required by the model to reproduce the data are rather less than the classical outer turning point, which is the region expected to be sampled in these experiments based on energy conservation and Franck-Condon considerations; as suggested below, this discrepancy probably arises due to exit channel effects, which are neglected in the model.

iii Experiments have also been performed on the HOD molecule prepared in OH stretching states $|40^{-}0\rangle$ and $|50^{-}0\rangle$, since it was anticipated that the OD photofragment population distributions would be more sensitive to variations in bending potential with H—OD bond extension than in the case of HOH. However, the internal state distributions of the OD photofragment (the only detectable product) are in much poorer accord with the predictions of the Franck-Condon model mentioned above. For H—OD photolysis, exit channel effects are expected to be more important than for H—OH, due to the shift in the centre-of-mass of the OD moiety relative to that of OH. This leads to an enhanced impulsive torque on the excited state surface as the fragments separate and simple impulsive type calculations suggest that such a torque would generate about one unit of angular momentum during dissociation. A modified Franck-Condon model which incorporates qualitatively this impulsive torque [8] provides much better agreement with the experimental data, and furthermore provides confirmation that dissociation out of $|50^{-}0\rangle$ at 282 nm does indeed take place close to the outer turning point of the bound state wavefunction [9]. Ironically, the data for the third overtone state are rather less well reproduced by the calculations: it may be significant that simple energetic considerations suggest that dissociation from this state at 282 nm must occur *outside* the classically allowed region of the bound state. It is hoped that more detailed 2D quantum calculations, which explicitly include the dynamics on the excited state surface (to be performed in collaboration with Dr D E Manolopoulos at Nottingham University), will confirm this picture in the near future and shed light on the

origins of more subtle discrepancies between the Franck-Condon calculations and experiment.

Quantum state resolved photodissociation dynamics of H_2O_2

The photofragmention of H_2O_2 is another process which has been extensively studied – experiments include direct photodissociation studies probing vector correlations in the recoiling OH fragments [10, 11] [3], the (rotationally unresolved) vibrationally mediated photodissociation (VMP) experiments of Crim and Coworkers [12] and fully quantum state resolved unimolecular dissociation studies on the ground state surface by Rizzo and Coworkers [13]. As with the water experiments outlined above, one of the objectives of this study was to probe the photofragmentation of H_2O_2 at the fully reagent and product quantum state resolved level, with particular emphasis on providing information on the *ro*vibrational dynamics in the bound state of hydrogen peroxide at high vibrational energies. Full reagent state selection was achieved by jet-cooling the parent molecule, thereby relieving spectral congestion in the overtone absorption spectrum.

Unlike the water experiments described above, the long wavelength vibrationally mediated dissociation of H_2O_2 *via* the third O—H stretching overtone ($4\nu_{OH}$) proceeds by cleavage of the HO—OH bond rather than that initially endowed with vibrational excitation (ie., the O—H bond). There is now a considerable body of both theoretical [14] and experimental [12] evidence to suggest that the OH photofragment yield in the VMP experiment is a sensitive indicator of the degree of O—O stretching character in the intermediate state, since it is amplitude of the bound state wavefunction along this coordinate which provides good Franck-Condon overlap with the excited state scattering wavefunction. In particular, in the absence of O—O stretching character in the intermediate state, no OH VMP signal would be detected at the dissociating photon energies ($\equiv$ 750 nm) employed in this study. The OH photofragment yield was therefore used to provide a signature of O—O stretching character in selected J_{K_a,K_c} states of $H_2O_2(4\nu_{OH})$, and hence to explore the role of molecular rotation in coupling the O—H and O—O stretching motions in the bound state of hydrogen peroxide at energies in excess

[3] The low lying excited electronic states of H_2O_2 are all strongly repulsive along the HO—OH coordinate.

of 13000 cm^{-1}.

OH VMP excitation spectral intensities derived from jet-cooled samples of H_2O_2 (and recorded on selected fragment rotational states in OH(v = 0)) were used to evaluate parent rotational state specific photodissociation cross-sections σ_{OO} [15], based on a knowledge of the primary photon absorption intensities σ_{OH}, which were available from a previous jet cooled absorption spectrum study by Douketis and Reilly [16] [4]. The following summarizes the principal conclusions from this investigation:

i Relative reagent rotationally state specific photodissociation cross-sections were found to vary by nearly two orders of magnitude between $J = 1$ and $J = 4$ and no VMP OH signal could be detected for parent molecules selected with $J = 0$. These data reveal that the detailed composition of vibrational overtone state of H_2O_2 is highly sensitive to parent rotation, and that the vibrational wavefunction for $J = 0$ is considerably more localized (presumably along the OH stretching coordinate) than for higher J. Given that the double resonance experiments of Rizzo *et al.* [17] suggest that the third OH stretching overtone state is probably $\geq 80\%$ OH stretching in character, for the comparatively high J values likely to be accessed in an (unresolved) thermal experiment, the present data indicate that the $J = 0$ vibrational motion must be highly OH local mode in character [15].

ii Parent molecular states with high components of the angular momentum about the a and b inertial axes were found to show the most pronounced enhancement in photodissociation cross-section, suggesting that molecular

[4]The absorption spectrum of H_2O_2 corresponding to excitation into the lowest symmetric torsional component of the third OH stretching overtone level (the level employed in the present experiments) is unperturbed for the low rotational states accessed, and both the intensities and line positions may be assigned on the basis of rigid asymmetric rotor simulations. This finding, together with the double resonance work of Rizzo and Coworkers [17], suggest that a single intermediate vibrational state is excited in these experiments and that its composition is $\sim 85 - 95\%$ local mode OH stretching in character. However, the presence of torsional hot and combination bands in the thermal VMP spectrum (and possibly in the jet cooled absorption spectrum as well) do suggest some coupling between the OH stretching and torsional motion at somewhat higher rovibrational energies.

rotation about these axes is particularly effective in promoting coupling between the O—H and O—O stretching coordinates [15]. The results are consistent with findings from both classical and quantum calculations [14], which indicate that O—H/O—O coupling is in fact indirect, mediated *via* coupling to the bending and particularly the torsional modes.

iii The relative photodissociation cross-sections were found to be insensitive to the rotational state selected in the *product* OH fragment. Furthermore, the OH $v = 0$ rotational state distribution obtained subsequent to dissociation of $H_2O_2(4\nu_{OH}, J_{K_a,K_c} = 2_{02})$ was remarkably similar to that obtained in thermal measurements, which are necessarily unresolved in reagent rotational state but are likely to proceed *via* much higher rotational states than accessed in the state selected jet-cooled measurements. Since the photofragment rotational populations reflect contributions from the bending and torsional motions in the intermediate state at large O—O bond extensions [18], it would appear that increases in the O—O stretching composition of the intermediate state with J are mirrored by similar increases in the amount of OOH bending and HOOH torsional character. Such a finding lends support to the conclusion (see item ii) that coupling between the OH and OO stretching modes is in fact indirect, mediated *via* coupling to the torsional and bending modes [15].

The $H + N_2O \rightarrow OH(X) + N_2$ *reaction*

One of the aims of this study is to exploit Doppler resolved laser induced fluorescence (LIF) probing techniques to obtain OH product state selective differential cross-sections and rotational polarizations using new strategies developed during the period of the grant by the investigator [19] in collaboration with Professor J.P. Simons [20], and concurrently by the groups of Bersohn [21], Zare [22], Hall [23] and Hancock [24]. The dynamics of this multi-channel reaction have been studied previously both in the gas phase and in van der Waals complex 'precursor geometry limited' experiments by Wittig and Coworkers [25], which employed photolysis of HI (at wavelengths between 193 nm and 266 nm) to generate the H atoms reagents. The OH reaction channel is believed to proceed by H atom attack at the terminal nitrogen atom forming an HNNO intermediate, which subsequently

undergoes H atom migration and dissociation to OH + N_2 products [25]. These conclusions were based partly on experimental OH internal state and translational energy release measurements (obtained using Doppler resolved LIF) [25], but the interpretation of the data is somewhat clouded by the use of HI as the H atom precursor molecule. At the photolysis wavelengths employed, both fast and slow H atoms are produced with significant quantum yield (corresponding to production of ground and spin-orbit excited state I atoms), separated in kinetic energy by $\sim$ 1 eV, and thus the reported OH reaction product internal state distributions and kinetic energy releases (obtained using Doppler resolved LIF techniques) have contributions from two markedly different reagent collision energies. Furthermore, the two photofragmentation channels are associated with different, near limiting translational anisotropies (of $\beta = -1$ and $+2$), and this too considerably complicates the interpretation of Doppler profile measurements.

The pump-probe experiments now being conducted use polarized laser photolysis of H_2S at 225 nm to generate comparatively monoenergetic, highly anisotropic ($\beta \simeq -1$) H atom reagents with kinetic energies in excess of 12000 cm^{-1} [26]. Data of sufficiently high quality to perform rotational alignment measurements, which place stringent constraints on the probe laser powers employable, have been obtained with total pressures of $\sim$ 100 mTorr and optical delay times of $\sim$ 20 ns [5] and the new experiments are already yielding some surprising results. The OH rotational state distribution in $v = 0$ (at a collision energy of 1.5 eV) is considerably colder than that observed previously (at collision energies of $\sim$ 0.95 and $\sim$ 1.9 eV) [25] and displays a clear preference for population of the lower spin-orbit state [27]. Furthermore, the OH product is endowed with lower degrees of vibrational excitation in the present 1.5 eV study. It would appear that the OH internal state distributions obtained by Wittig and Coworkers are dominated by contributions from the higher (1.9 eV) collision energy, suggesting that the excitation function for the reaction increases with collision energy, consistent with proposed barriers either to direct H atom attack at the oxygen atom, or to H atom migration subsequent to attack at the terminal nitrogen atom [28]. Work is currently in progress to

[5] At a delay time of 20 ns the product of the pressure times the time delay is $\sim 2 \times 10^{-9}$ Torr sec at 100 mTorr pressure, well below the values frequently employed in similar 'single collision' experiments [25].

obtain specific OH LIF features under Doppler resolution, from which differential cross-sections and polarization information can be obtained. Simulations indicate that although the kinematics of the reaction are not ideal for extracting differential cross-sections, Doppler profiles taken in alternative pump-probe geometries and on different rotational branches will be very sensitive to the degree of sideways versus forward and/or backward scattering and hence provide detailed product state selective information about the nature of the HNNO intermediate implicated in the reaction mechanism [25].

Publication and Dissemination of Results

The research outlined above has thus far lead to the four papers (two published and two in preparation) listed in the section below in bold face. In addition, the work has been presented at National meetings of the Molecular Beams and Dynamics (in 1993 and 1994) and the Gas Kinetics (in 1994) Discussion Groups of the Royal Society of Chemistry and will be presented at the 'International Conference on the Dynamics of Molecular Collisions' in California this summer. The research has also been the subject of invited seminars in Oxford and Nottingham and at the University Complutense, Madrid, and Cornell University in 1994.

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