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the relative importance of competing mechanisms in such reactions. An exact treatment of these phenomena can be obtained by extending the analysis from contracted states to the full continuum of states and employing path integral methods; this extension will be described in subsequent papers.

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[9] A potential difference of only one unit of $k_B T$ may seem unrealistically soft. However, in contracted models such as these, the energies considered are actually free energies. The large entropy in the plateau region of Fig. 2 could substantially lower the free energy of contracted state 2 relative to states 1 and 3.

Polarized LIF spectroscopy of OH formed by the photodissociation of H2O by polarized 157 nm light

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Macpherson, Simons, and Zare[1] have described "polarized photofluorescence excitation spectroscopy," in which a molecule ABC is dissociated by linearly polarized light into AB^* and C and the polarization of the subsequent fluorescence is analyzed. We discuss here results from a related technique in which ABC are similarly *photodissociated* but to *products in the ground electronic state*. The AB is analyzed with the use of a polarized probe laser, i.e., polarized laser induced fluorescence (PLIF).[2] Photodissociation to AB often involves simpler steps than those to AB^*. Water was used because (a) it is suitable for theory, (b) we expected large polarization effects, and (c) the H_2O^* state $(\tilde{A}\,^1B_1)$[3] dissociates directly and rapidly with 2.7 eV excess energy.

The basic ideas follow. Water is dissociated by an excimer laser, at 157 nm, whose output is linearly polarized by a Rochon prism. The H_2O transition moment μ_D is perpendicular to the molecular plane.[4] The probability of excitation to H_2O^* is $\propto |\epsilon_D \cdot \mu_D|^2$, where ϵ_D is the laser's electric vector. The H_2O^* planes are then preferentially aligned perpendicular to ϵ_D. The forces acting in the dissociation lie in these planes and so the J vectors of the OH are partially aligned with ϵ_D. A dye laser is linearly polarized by a Glan–Thompson prism and its electric vector ϵ_E can be turned with a $\lambda/2$ plate. It is tuned to excite individual J levels, using Q-branch transitions, where classically, the transition moments μ_E are parallel to J,[5] so that the number of

OH* and the PLIF intensity are largest when $\epsilon_D \parallel \epsilon_E$, and smallest when $\epsilon_D \perp \epsilon_E$. From these intensities the anisotropy in the dissociation process can be measured. The OH is analyzed for alignment, in both $\Pi_{1/2}$ and $\Pi_{3/2}$ states, at $v'' = 0$, at each J.

The apparatus, with the exception of the polarizing optics and a pulsed molecular beam, is similar to one previously described.[6] Briefly, the two laser beams are coaxial and antiparallel. The excimer light is usually 50–100 ns before that of the probe. Both pulses are ~10 ns long. The water is either (a) in the form of a pulsed nozzle beam or (b) as 300 K vapor at submicron pressures. Part of the LIF light is directed into a photomultiplier whose output goes to a boxcar integrator.

Both ϵ_D and ϵ_E can be adjusted to be either vertical or horizontal. The possible cases are (a) $\epsilon_D \parallel \epsilon_E \parallel y$, (b) $\epsilon_D \parallel y$ and $\epsilon_E \parallel z$, (c) $\epsilon_D \parallel z$ and $\epsilon_E \parallel y$, and (d) $\epsilon_D \parallel \epsilon_E \parallel z$, where x, y, and z are as shown in Fig. 1. Cases (a) and (d), and (b) and (c), are not equivalent because the fluorescence is anisotropic (see below).

We assume that photodissociation yields a distribution of J vectors which is $\propto [1 + \beta P_2(\cos\theta)]$, where $P_2(\cos\theta) = (3\cos^2\theta - 1)/2$, β is an anisotropy parameter and θ is the angle between ϵ_D and J. For $\beta = 2$, this reduces to a $\cos^2\theta$ distribution. For our classical analysis $\mu_E \parallel J$, so that the excitation probabilities are $\propto |\epsilon_E \cdot J|^2$. The fluorescence consists of unresolved P, Q, and R lines. The P and R lines emit radiation with the same angular
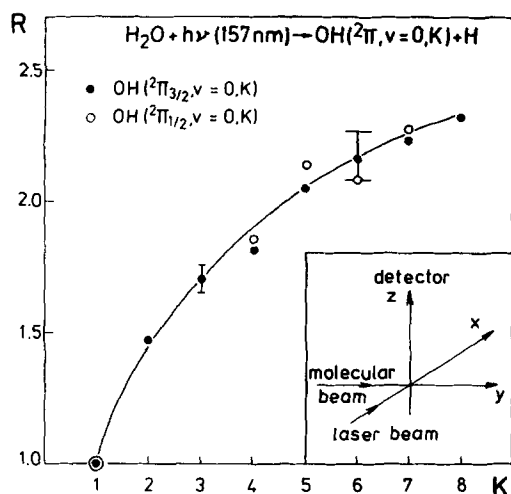
FIG. 1. Average values for experimental LIF intensity ratios R [case (a)/case (b)] as a function of quantum number K. Case (a) has $\epsilon_D \parallel \epsilon_E \parallel y$ and case (b) has $\epsilon_D \parallel y$ and $\epsilon_E \parallel z$, where the coordinates are shown in the inset. The OH is pumped from the $X\,^2\Pi_i$ to the $A\,^2\Sigma^+$ state, with $v'' = v' = 0$. The line serves to connect points, and is not theory. Error bars represent standard deviations. These data are for water vapor.

dependence, but Q radiation is different.[5,7] With methods analogous to those described in Refs. 7 and 8, we derived expressions for the PLIF. For both Q, P, and R lines we calculated the joint angle-dependent probability of (a) forming OH with a particular J direction, (b) of exciting that OH with a Q transition, and (c) finding the components of the rotation-averaged emission dipole on x, y, and z. We integrate over all solid angle and then average the Q, and P and R contributions. (The sum of the P and R intensities equals that of the Q.)

These calculations yield the emission components I_x, I_y, and I_z. The PLIF at the detector is $\propto (I_x + I_y)$ and for our four cases, the normalized $I_x + I_y$ are (a) $7 + 41\beta/14$, (b) $6 - 15\beta/14$, (c) $7 - 11\beta/7$, and (d) $6 + 15\beta/7$. Most of our data are ratios R of case (a)/case (b) and case(d)/case (c).

We did experimental checks (a) to assure that our level of stray magnetic fields is unimportant, (b) that values for β found with various R for the four cases are consistent, and (c) that the use of P or R line excitation leads, as expected, to much smaller R. Particular care was required to have the probe laser intensity so low that further reduction does not change R. We usually attenuated by a factor of 100.

Figure 1 displays experimental ratios R for case (a)/case (b) as a function of quantum number K for both the $\Pi_{1/2}$ and $\Pi_{3/2}$ states, for which $J = K - \frac{1}{2}$ and $K + \frac{1}{2}$, respectively. The most striking feature is the large value of R for high K. For $R = 2.3$, for example, $\beta = 1.26$. These R can be compared to polarization effects of $\sim 0\%-10\%$ found in polarized photofluorescence excitation spectroscopy. Our large R are caused by excitation to a single repulsive potential surface which leads to a fast direct dissociation. In contrast, photofluorescence cases often involve excitation to mixed states and/or predissociation. While our anisotropy is large,

R does not approach the 10/3 value that would be predicted if $\beta = 2$, i.e., if the J were to retain the $\cos^2\theta$ distribution in the initially excited H_2O^*. This is because the H_2O^* planes rotate. In-plane rotations do not reduce R, but the out-of-plane do.[9,10] In the dissociation, the initial H_2O rotation slows down and finally stops as the H–OH distance increases and a final stationary H_2O plane is reached.

Figure 1 also displays an increase of R with K. At the lowest K, nonclassical behavior accounts for part of this increase. However, quantum calculations of the degree of polarization for Q excitation, and for (a) Q fluorescence, approach the classical limit, within our experimental precision, by $J = 3.5$, while those for (b) P or R fluorescence approach their individual limits more slowly, but their average, which is needed here, is adequate by $J = 3.5$.[7,11] Thus the increase at the lower K is only partially attributable to quantum effects, and the remainder, and that at larger K, is due to the dynamics of the process. The dynamics are still under investigation.

Higher R values are obtained with pulsed molecular beams. Interpretation here is more complicated, because of (a) alignment of H_2O in the beam and (b) the very rotationally cold water molecules. Further experiments are in progress to sort out these effects. However we have established that the cold water reduces the rotational depolarization.

In summary, we have produced very large alignment effects in photodissociation of H_2O. For larger J's, the observations can be explained with the assumption of an anisotropy factor in the dissociation and a classical dipole model. The large effects are clearly due to a simple excitation and direct dissociation. Further experiments are in progress with both vapor and beams.

[a] Guest at MPI für Strömungsforschung, where the experiments were conducted.

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