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Control of fragment alignment via photodissociation from different types of parent rotation

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The alignment of the OH fragment following dissociation of H_2O (1,0,0) at 193 nm has been measured as a function of initially prepared parent rotations. The degree of alignment is almost perfect for an in-plane rotation, but is reduced markedly for a mixture of in- and out-of-plane rotations.

A detailed understanding of the photodissociation dynamics in a molecule must include not only the overall scalar properties such as internal state distributions, but also the vector properties such as rotational alignment of the photofragments.¹⁻⁵ Therefore, experimental photodissociation studies usually include measurements of scalar and vector observables. Internal state distributions of the fragments formed in the photodissociation of state selected parent molecules have recently been reported for several systems.⁶ However, vector properties of the fragments have less frequently been measured. It is evident that measurements of vector properties in experiments where parent molecules are prepared in particular rotational states may provide additional insight into the dynamics of the dissociation events.

The effect of parent rotation on the direction of fragment recoil and rotational alignment is discussed in Refs. 7-9, respectively. However, very limited experimental information exists on the effect of parent rotation on alignment. Andresen et al.¹⁰ studied the influence of parent rotation in photodissociation of water in the first absorption band by cooling the molecules and obtaining a higher degree of alignment than in molecules dissociated at room temperature. Hodgson et al.¹¹ measured the rotational alignment via photofragment fluorescence in the state selected predissociation of H₂O and D₂O from the $C^{1}B_{1}$ state and used it as an aid in assignment of the underlying continuum. Also, vector correlations were studied by Brourad et al.¹² in the vibrationally mediated photodissociation of H₂O₂ by exciting rotations that correspond to particular K_a sub-band features. They found that none of the correlations are sensitive to parent molecular levels.

Nevertheless, the effect of different types of parent rotations (in-plane vs out-of-plane) on vector properties, has not been directly demonstrated for specific rotational states. In the present Communication we report on the first *direct* demonstration of the effect of particular parent rotations on fragment alignment. This is carried out via state selected detection of OH, obtained from 193 nm photodissociation of particular rotational states of the symmetric stretch vibration of water, H_2O (1,0,0). The alignment is measured by varying the polarization of the probe laser relative to that of the dissociating laser. It is shown that the rotational alignment of the OH fragments strongly depends on the initial rotational state of water and that the degree of alignment is almost perfect for an in-plane rotation, but reduced markedly for a mixture of in- and out-of-plane rotations.

The experimental approach and apparatus are similar to that previously employed,¹³ with the addition of polarization optics for the dissociating and probe lasers. Briefly, stimulated Raman excitation (SRE) and coherent anti-Stokes Raman scattering are used to prepare and detect, respectively, particular rotational states of H_2O (1,0,0). The excitation is effected with two visible beams, the second harmonic of a Nd:YAG laser 532 nm (\sim 50 mJ) and a tunable dye laser pumped by it, operating around 660 nm $(\sim 5 \text{ mJ})$. Both beams are parallelly polarized, collinearly combined, overlapped spatially and temporally, and focused into the cell. The dye frequency is tuned so that the frequency difference of the two lasers scans through the Q-branch transition of H_2O (1,0,0).¹⁴ Two different transitions which prepare the initial states of H₂O are chosen: one prepares the 3_{03} state which is pure in-plane¹⁵ rotational state and the other a mixture of the $3_{21}+3_{22}+4_{14}$ states with about equal weights of in- and out-of-plane rotations (the exact weight is not known because of the insufficient resolution and the SRE saturation). Pure outof-plane rotations could not be utilized in the experiments since they are too weak or not resolvable.^{13,14} Following the excitation, after 25 ns, the rovibrational excited molecules are photodissociated by a 193 nm beam from an ArF excimer laser (~ 1 mJ). The photodissociating beam is polarized by a quartz double prism Rochon polarizer [which allows the use of either P (o ray) or S (e ray) polarization direction, ϵ_{p} and then enters the reaction cell counterpropagating the SRE beams. The frequency doubled output beam of a Nd:YAG-pumped dye laser around 282 nm is used for laser induced fluorescence (LIF) detection of the OH fragments on the A, $v'=1 \leftarrow X$, v''=0transition,¹⁶ after an additional delay of 25 ns. The probe beam passes through an Archard-Taylor polarizer and a $\lambda/2$ retarder (two Fresnel Rhombs), which allows rotation of its polarization direction, ϵ_a . It then enters the reaction cell collinearly with the SRE beams. The pulse energy of the probe laser is attenuated to $\sim 0.1 \ \mu J$ in order to preclude saturation of the LIF signal. The LIF signal is detected at a right angle of the laser beams with a photomultiplier equipped with an interference filter $(314 \pm 5 \text{ nm})$ and imaging optics that is insensitive to the polarization.

The LIF intensity due to photodissociation can be written as 17

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$$I \propto P(J) B[q_0 + q_2 A_0^{(2)}], \qquad (1$$

where P(J) is the fragment population in the state J, B the transition probability, q_0 and q_2 are parameters that depend on the transition and on the experimental geometry, and $A_0^{(2)}$, the alignment parameter, measures the correlation between the parent transition dipole moment, μ , and the fragment's angular momentum, J. $A_0^{(2)}$ is determined from the variation of the line intensities in two geometries with $\epsilon_a \perp \epsilon_p$ and $\epsilon_a \parallel \epsilon_p$. Also, experiments in which the direction of ϵ_p is rotated by 90° relative to the polarization direction of the SRE beams, with $\epsilon_a \perp \epsilon_p$ and $\epsilon_a \parallel \epsilon_p$, are conducted to check possible alignment of the H₂O molecules (due to SRE excitation) before dissociation.

The initial rotational states of H₂O are prepared by SRE using parallel polarized beams. Therefore, the degree of alignment of the initially prepared H₂O states has to be examined. Such alignment, if it exists, would affect the subsequent photodissociation dynamics and should be considered in the analysis. For parallel polarized beams, the Raman transition has contributions from both the isotropic and the anisotropic terms of its polarization tensor.¹⁸ However, for $H_2O(1,0,0)$ the anisotropic term is negligible and all the transitions belong to the isotropic Q branch.¹⁴ Transitions of this branch are not expected to result in an anisotropic distribution of the prepared molecules^{19,20} prior to the photodissociation. Moreover, the measured alignment for photodissociation of molecules with ϵ_p at 90° and 0° (with $\epsilon_a \perp \epsilon_p$ and $\epsilon_a \parallel \epsilon_p$) relative to the polarization of the SRE beams is similar within experimental error. Therefore, any initial alignment (if it exists) is negligible, allowing the utilization of the usual Greene and Zare treatment.17

The experiments are conducted in a gas cell through which the sample flows at a pressure of 100 mTorr. The pressures and delays used in the experiments minimize collisional relaxation of the initially prepared rotational states of the H_2O and the rotational states of OH.¹³

Figure 1 shows a part of the OH LIF spectra resulting from the photodissociation of the 3_{03} rotational state of H₂O (1,0,0) obtained in two experimental geometries as indicated in the insets. It is clearly seen that the main *Q*-branch lines are larger relative to the *P* and *R* lines in the case for $\epsilon_a \parallel \epsilon_p$ [panel (a)] compared to the case for $\epsilon_a \perp \epsilon_p$ [panel (b)]. A similar behavior, but much less pronounced, is observed for the photodissociation of the second state which consists of the $3_{21}+3_{22}+4_{14}$ rotational states. One can conclude from this behavior that J is aligned preferentially parallel to $\mu(A_0^{(2)} > 0)$ even before the calculation of $A_0^{(2)}$ described below.

The intensities of the excitation spectra in the two geometries are first normalized according to the procedure used in Ref. 21, and then the values of $A_0^{(2)}$ as a function of *J* are obtained from the ratio of the intensities of the *Q* lines (which are the most sensitive to the experimental geometry^{10,17,21}). The resulting values for the photodissociation of the 3₀₃ (closed circles) and the 3₂₁+3₂₂+4₁₄ (open squares) rotational states of H₂O (1,0,0) are shown in Fig. 2. Also shown in Fig. 2 are (1) limiting values of $A_0^{(2)}$ in



FIG. 1. A part of the LIF excitation spectra of the OH photofragments (measured via the A, $v'=1 \leftarrow X$, v''=0 transition and assigned according to Ref. 16) resulting from the photodissociation of the 3_{03} rotational state of H₂O (1,0,0), with (a) $\epsilon_a \parallel \epsilon_p$ and (b) $\epsilon_a \perp \epsilon_p$. The fluorescence is detected along the Z axis by a detection system that is insensitive to polarization.

the high-J limit (represented by the solid line at 0.8) and (2) calculated values based on a classical model (dashed line) which assumes completely planar dissociation and includes depolarization effects due to A-doubling mixing and hyperfine structure.¹⁰ It is clearly seen that the measured values of $A_0^{(2)}$ increase with J for dissociation from both states and show a similar trend to that obtained from the theoretical values. However, the degree of alignment obtained for the photodissociation of parent molecules prepared in the in-plane rotational state, 303, is higher (a factor of two for J=5.5) than in the mixed in- and out-ofplane state which contains the rotations $3_{21}+3_{22}+4_{14}$. Also, the experimental value of $A_0^{(2)}$ for the 3_{03} state at the highest J is in good agreement with the calculated value. Yet the experimental points increasingly deviate from the expected alignment as J decreases (see below).

The explanation for the above observations is depicted in Fig. 3, which is a classical description of a completely planar dissociation of H_2O and of the OH fragments LIF detection. Also shown is the geometry of the experiment 4220



FIG. 2. The OH photofragment alignment parameter, $A_0^{(2)}$ as a function of *J*, obtained for the photodissociation of H₂O (1,0,0) molecules initially prepared in 3₀₃ (closed circles) and 3₂₁+3₂₂+4₁₄ (open squares) rotational states. The solid line represents the limiting value of $A_0^{(2)}$ and the dashed curve is the result of calculation on the basis of the classical model corrected for depolarization effects arising from Λ -doubling mixing and hyperfine structure.

including the polarizations (ϵ) and the propagation directions (**k**) of the lasers used in the experiments. The transition moment for the 193 nm $A \leftarrow X$ excitation of H₂O is perpendicular to the H₂O plane,^{10,22} hence molecules lying in a plane perpendicular to the direction of ϵ_p are preferentially dissociated.¹⁻⁵ After fragmentation, the OH products rotate in the H₂O plane leading to the alignment of J parallel to ϵ_p and to $A_0^{(2)} > 0$. Out-of-plane rotation of the parent (indicated by the *out* arrows in Fig. 3), results in reduction of the alignment. The degree of this reduction depends on the rotational period and on the fragmentation time. The OH transition moment, μ_{OH} , is perpendicular to



FIG. 3. Schematic picture of the high-J limit classical description of the photodissociation process and LIF detection of the fragments in two experimental geometries. Shown are the relative directions of μ , the transition moments of H₂O and of OH Q and P/R lines, and J the OH rotational vector. Also depicted are the k vectors and the polarization directions ϵ of the photolysis (subscript p) and probe (subscript a) lasers. The arrows in and out describe in- and out-of-plane rotations of H₂O, respectively.

the internuclear axis and perpendicular to or rotating in the OH plane of rotation for Q or P/R lines, respectively. This leads to an opposite behavior of the Q or P/R lines in the two experimental geometries with $\epsilon_{a} \perp \epsilon_{p}$ and $\epsilon_{a} \parallel \epsilon_{p}$.

The main approximations of this classical picture are the assumptions that J is perpendicular to the OH rotational plane and that μ_{OH} is perpendicular or parallel to this plane. These approximations are only good in the high-J limit¹⁰ which is not achieved for the OH rotational states detected here. Due to Λ -doubling mixing at low J's, $\mu_{\rm OH}$ is neither perpendicular nor parallel to the OH rotational plane, but makes a J-dependent angle relative to it.^{10,23} This depolarization effect results in reduction of the measured alignment, and it is taken into account together with the depolarization from the OH hyperfine structure¹⁷ in the classical theoretical values depicted in Fig. 2 (dashed curve). The increasing deviation of the calculated from the measured alignment for decreasing J is due to the classical treatment and to the partial overlap of the main Q_1 and satellite Q_{21} lines in our experiment (see Fig. 1). The overlap leads to depolarization^{10,21} since the satellites belong, in terms of ΔJ , to the P branch.^{10,16} The depolarization increases as J decreases since low J lines tend to be more overlapped. However, from the agreement between the measured (for photodissociation from the 3_{03} state) and calculated alignments, in particular for J=5.5 which is the highest measured J, it is deduced that the dissociation is very close to being completely planar. The lower alignment measured for the photodissociation of the $3_{21}+3_{22}$ $+4_{14}$ state is a direct consequence of the out-of-plane rotation component of this mixed state.

To conclude, our results directly demonstrate the importance of the type of parent rotation on vector properties. For photodissociation of the parent in-plane rotation (the 3_{03} state) the maximum attainable alignment is observed for the highest measured J and about half of it is lost for the photodissociation of the mixed rotation (the 3_{21} $+3_{22}+4_{14}$ state). Hence, these observations confirm the assumption that out-of-plane rotations are responsible for alignment loss. Such studies of alignment in state-to-state photodissociation experiments can be extended to extract other vector correlations. In particular, by preparing a pure in-plane rotation one can preclude the effect of the out-of-plane rotations which is detrimental for measurements of vector correlations at room temperature. Higher resolution lasers are needed for preparing a number of single rotational levels (pure in-plane, pure out-of-plane, and intermediate states) of the parent to enable a more quantitative analysis. Also, the preparation of photofragments with preferred alignment may serve as a source for aligned radicals for reaction dynamics studies.

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