

## Strong propensity rules in the photodissociation of a single rotational quantum state of vibrationally excited H<sub>2</sub>O

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ing the three  $P(3,K)$  lines of  $\text{H}_2\text{O}^+$  predicted by Liu and Oka<sup>1</sup> and Sears<sup>10</sup> to lie between 360 and 400 GHz.

**Note Added in Proof:** After submission of this manuscript we have learned that Bogey *et al.* (Astronomy and Astrophysics, July 15, 1985), has measured the 3  $P(3, K)$  lines of  $\text{H}_2\text{O}^+$  in the laboratory.

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## Strong propensity rules in the photodissociation of a single rotational quantum state of vibrationally excited $\text{H}_2\text{O}$

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The photodissociation of  $\text{H}_2\text{O}$  in the first absorption band is an ideal process to understand the basic principles of simple fragmentation phenomena.<sup>1</sup> The only products are OH and H, both in their electronic ground states. There is only a single, well isolated, strong repulsive potential surface involved and the process is fast and direct. With modern quantum methods this fragmentation can be studied on an *ab initio* basis in great detail,<sup>2,3</sup> and theoretical predictions can be compared with experimental results.

In the experiment reported here, a *single rotational state* in an excited vibrational state is prepared with a tunable IR laser. This allows variation of the initial state, as well as complete definition. The photodissociation of *single quantum states* yields pronounced oscillations in the OH product state distributions. The surprisingly different results, compared to the photodissociation of 10 K cold  $\text{H}_2\text{O}$ ,<sup>1</sup> are due to the even better state preparation here.

The IR excitation is done in the range of the symmetric and antisymmetric stretch at  $2.7\ \mu$ , where water has a strong absorption band.<sup>4</sup> The IR laser is an excimer-pumped dye laser, whose output is Stokes shifted. The third Stokes gives 0.5 mJ. About 50 ns after the IR excitation an ArF excimer laser is fired. The absorption cross section of  $\text{H}_2\text{O}$  at 193 nm is very small and direct photolysis at 193 nm with 300 mJ pulse energy gives little OH signal. However, because the vibrationally excited state has  $\approx 0.5$  eV more energy, the absorption cross section of the vibrationally excited state  $\text{H}_2\text{O}$  is estimated  $\approx 500$  times larger. Even considering the partitioning function, this implies smaller signals from direct photolysis than for that from the vibrationally excited state. The OH state distribution is analyzed by LIF.

Except for the IR laser, the experiment is similar to that described previously.<sup>5</sup> It is essentially an  $\text{H}_2\text{O}$  flow system with a collinear arrangement of the three laser beams. IR

and excimer laser are unpolarized. The typical delays were 50 ns between the IR, ArF, and OH probe lasers at pressures near 0.04 Torr. Rotational distributions were identical for smaller pressures and shorter delays.

Some results are shown in Fig. 1. The upper trace in Fig. 1(a) shows an IR-photoacoustic spectrum of  $\text{H}_2\text{O}$ , recorded with a microphone. When the frequency matches a transition in  $\text{H}_2\text{O}$ , a sound wave is emitted and is received at the microphone. The peaks were identified using the well-known IR spectrum of  $\text{H}_2\text{O}$ .<sup>6,7</sup> The labels at the lines are *rotational* quantum numbers: the upper label is for the vibrationally excited stretch and the lower label is for the vibrational ground state. The lower trace is recorded in a completely different way: we tune the OH probe laser to a known transition, in this case the  $R_{11}$  line. The IR laser is scanned over the same frequency range as before, with the ArF laser firing between the other lasers. We obtain OH fluorescence at exactly the same IR frequencies. Clearly these peaks demonstrate photodissociation from different IR excited rotational states.

Figure 1(b) shows rotational distributions for different fine structure components of the OH fragment after the photodissociation of the rotational state  $4_{04}$  in the asymmetric stretch mode. In this case the IR laser excites the  $4_{04}$  state, indicated by the arrow in Fig. 1(a). The photolysis is done at 193 nm, and the OH probe laser is scanned to measure the OH rotational distribution. Shown are the distributions for both  $\Lambda$  doublets, i.e.,  $\Pi^-$  and  $\Pi^+$ , in  $^2\Pi_{3/2}$  and  $\Pi^-$  in  $^2\Pi_{1/2}$ .  $\Pi^+$  in  $^2\Pi_{1/2}$  has not been measured because of line overlaps. Arbitrary units are used, but the relative heights of the curves are correct.

The rotational distributions are completely non-Boltzmann and show an oscillatory behavior with  $\Delta N = 1$ , at least at lower  $N$ . With increasing  $N$  this effect is less.

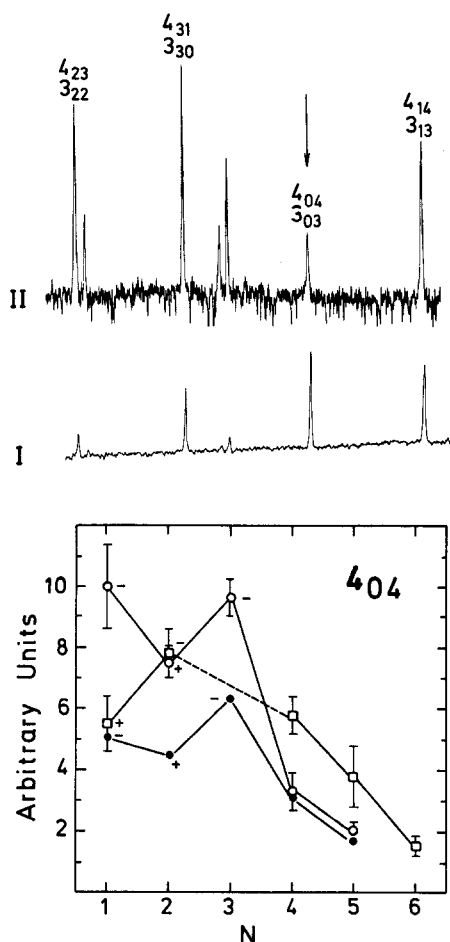


FIG. 1. (a) IR spectrum of the asymmetric stretch of  $\text{H}_2\text{O}$  between 3834.5 and 3844.5  $\text{cm}^{-1}$ . The upper and lower labels represent the upper and lower rotational quantum numbers  $J, K_a, K_c$  of the transition. I is the change of the OH R,1 LIF signal. II is the microphone output caused by IR water adsorption. (b) Rotational distribution of the OH fragments found in the photolysis of water out of the rotational state  $4_{04}$  of the asymmetric stretch.  $N$  is the total angular momentum of OH without spin. The open circles are for the  $^2\Pi_{3/2}^-$  state, the open squares are for the  $^2\Pi_{3/2}^+$  state, and the full circles are for the  $^2\Pi_{1/2}^-$  state. The  $N = 3$  state in  $^2\Pi_{3/2}^-$  could not be measured because of line overlap. The  $+/-$  symbols are the total parities for a given final OH state.

The distributions of the  $\Pi^-$  states of  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  are very similar. If the degeneracy is taken into account they are almost identical, which indicates a statistical spin popula-

tion. This also demonstrates that the oscillatory structure is real.

A comparison of the distributions for the two  $\Lambda$  doublet states in  $^2\Pi_{3/2}$  shows that the oscillations are out of phase: the population for one  $\Lambda$  doublet increases when the other decreases.

Although the distributions are very different, there is a common result: states with total parity  $P = -1$  dominate. The total parity  $P$  is shown in Fig. 1(b) for each state. For a given  $\Lambda$  doublet state,  $P$  changes with  $\Delta N = 1$  because the parity for nuclear rotation changes.<sup>8</sup> The two  $\Lambda$  doublet states have opposite parities for a given  $N$ . Thus the peaks in the distributions always correspond to  $P = -1$ . Photodissociation from other rotational states also shows oscillatory behavior.<sup>9</sup> These distributions are, however, very different, depending upon the initially prepared quantum state.

The origin of the strong dominance for the total parity  $-1$  is not yet understood. Nevertheless, we obviously have a propensity rule with an approximate conservation of symmetry. Such propensity rules are very common phenomena in heavy nuclear dynamics, if particles with internal electronic structure are involved.<sup>10</sup> The above results are just one nice example for a strong propensity rule in photodissociation.

The experiment demonstrates that photodissociation of single, selectable states is possible and yields new insight into fine details of simple fragmentation processes.

<sup>a)</sup> Guest at MPI, where experiments were done.

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