

# Photodissociation of Single H<sub>2</sub>O Quantum States in the First Absorption Band: Complete Characterization of OH Rotational and $\Lambda$ -Doublet State Distributions

R. Schinke, V. Engle, P. Andresen, and D. Häusler

*Max-Planck-Institut für Strömungsforschung, D-3400 Göttingen, Federal Republic of Germany*

and

G. G. Balint-Kurti

*School of Chemistry, Bristol University, Bristol BS8 1TS, United Kingdom*

(Received 24 June 1985)

A complete characterization of rotational and electronic fine-structure-state distributions of the product OH from photodissociation of H<sub>2</sub>O in the first absorption band is presented. Vibrationally excited water molecules are prepared in a well-defined rotational state by ir excitation, and photodissociation of this state is studied. The theory is based on numerically exact wave functions for ground-state water; the dissociative wave function is expanded in terms of OH(<sup>2</sup>Π) wave functions (including electronic structure) and inelastic effects in the excited state are shown to be negligible. The comparison between theory and experiment is quantitative on the basis of six quantum numbers.

PACS numbers: 34.50.Pi, 82.50.Et

Recent years have witnessed growing interest in the understanding of photodissociation processes in small molecules. Modern laser methods allow true state-to-state experiments, which were not possible some years ago,<sup>1</sup> and detailed dynamical methods have been devised<sup>2</sup> to interpret such experiments. While considerable progress has been made in the understanding of the observations which result from modern photodissociation experiments, we believe that the comparison presented in this Letter represents the most detailed theoretical characterization yet achieved of an experimentally observed product-state distribution. The dynamical treatment used contains absolutely no adjustable parameters.

A quantitative comparison of a state-to-state experiment with *ab initio* theory is reported for the photodissociation of H<sub>2</sub>O in its first absorption band. This is one of the fortunate cases, where a particularly clear and simple situation is encountered and accurate quantum calculations are feasible. There is only one excited-state potential-energy surface involved, which has been determined by Staemmler and Palma.<sup>3</sup> Because of the repulsive nature of the surface no predissociation occurs. A series of experimental<sup>4,5</sup> as well as theoretical studies (neglecting the electronic structure of OH)<sup>6,7</sup> have already lead to promising agreement of experiment and theory.

The completely state-to-state experiments reported here show unusual product quantum-state distributions. The experimental setup is described elsewhere.<sup>5</sup> By use of a tunable ir laser H<sub>2</sub>O is vibrationally excited to a single rotational state. The photodissociation of this quantum state is studied at 193 nm and the nascent OH product-state distribution is analyzed by laser-induced fluorescence. The measured quantum-

state distributions are obtained for the  $\nu_1 = \nu_2 = 0$ ,  $\nu_3 = 1$  state of H<sub>2</sub>O with total angular momentum  $J_i = 4$  and different projection quantum numbers.

We note the following observations: (1) The rotational-state distributions for a given  $\Lambda$  doublet are considerably structured (see Fig. 1). (2) The oscillations are in opposite sense for different  $\Lambda$ -doublet states (see Fig. 2). (3) For a given  $\Lambda$  doublet and rotational state the spin states are approximately populated according to their statistical weights. (4) The distributions depend sensitively upon the initially prepared quantum state of H<sub>2</sub>O. All of these findings, which are at first glance surprising, are (almost) quantitatively explained by the following theory.

The detailed cross section for dissociation of the initial state  $i$  of H<sub>2</sub>O into a final state  $f$  of OH is proportional to the square of the three-dimensional overlap integral

$$\langle \Psi_{\text{g.s.}}^i | \mu_e | \Psi_{\text{ex}}^f \rangle \quad (1)$$

over the ground-state wave function  $\Psi_{\text{g.s.}}^i$ , the scattering wave function  $\Psi_{\text{ex}}^f$ , and the transition dipole moment  $\mu_e$ . The final quantum-state distributions of the molecular fragments are mainly determined by three effects: (1) the initial preparation of the system in its excited electronic state, i.e., the projection of  $\Psi_{\text{g.s.}}$  onto the upper electronic potential-energy surface (Franck-Condon principle); (2) the inelastic scattering in the excited (dissociative) electronic state; and (3) the asymptotic translational energies of the molecular fragments in their various quantum states, which determine the classical turning-point region and thereby the overlap of the continuum wave functions with  $\Psi_{\text{g.s.}}$ . Relatively few detailed analyses of molecular photodissociation processes have been presented.<sup>2</sup>

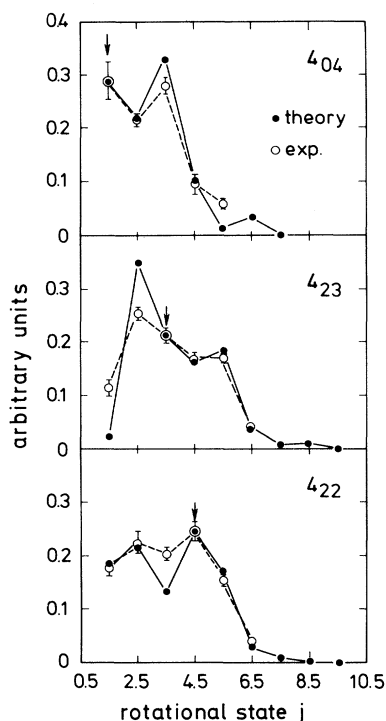


FIG. 1. Rotational-state distributions within the lower  $\Lambda$ -doublet state of the  $2\Pi_{3/2}$  manifold for three rotationally excited levels of water. The arrows indicate the rotational states where theory and experiment are normalized.

The most difficult aspect of any such analysis relates to the second of these effects. In many cases the "final-state interaction" is simply ignored, while in others assumptions are made as to the form of the excited potential-energy surface to permit the calculation of these effects.

In the case of the first absorption band of water, an accurate *ab initio* potential-energy surface for the upper electronic state has been calculated.<sup>3</sup> This permits a rigorous dynamical analysis of the final-state interaction to be undertaken.<sup>6</sup> In a recent investigation<sup>7</sup> we have shown that rotationally inelastic effects are negligibly weak for this system because the ground- and excited-state potential-energy surfaces have roughly the same equilibrium angle and the angular and radial motions on these surfaces are almost completely decoupled.<sup>7</sup> Since the energetic effects on the product-state distribution (effect 3) are also small for low initial rotational levels, the final product quantum-state distributions are primarily determined by the Franck-Condon projection of the initial state onto the asymptotic fragment product quantum states.

For a quantitative comparison with experiment, the inclusion of the electronic structure of the products, which in most cases have open shells, is important. Although in previous treatments this has been neglect-

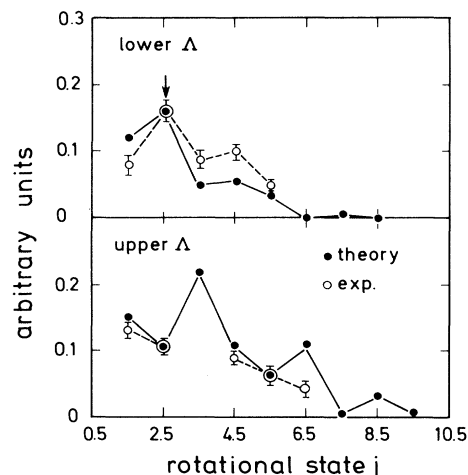


FIG. 2. Rotational-state distributions within the lower and the upper  $\Lambda$ -doublet states of the  $2\Pi_{3/2}$  manifold for the  $4_{14}$  level of water. The arrow indicates the rotational state where theory and experiment are normalized. The same normalization factor is used in both cases.

ed, it turns out to be important for a complete characterization of our water data. The electronic structure of the  $\text{OH}(^2\Pi)$  product is included following the recent work of Balint-Kurti.<sup>8</sup> The basic idea is to expand the wave functions in terms of asymptotic product eigenfunctions, taking into account spin and  $\Lambda$ -doublet states of  $\text{OH}$  as well as the spin of the  $\text{H}$  atom. With neglect of inelastic effects, this leads to a compact expression for the probability of finding  $\text{OH}$  in different

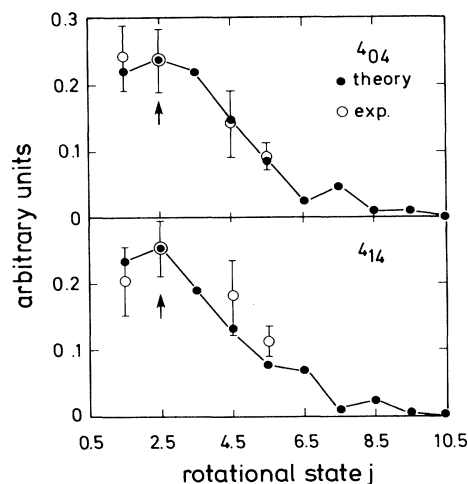


FIG. 3. Rotational-state distributions within the  $2\Pi_{3/2}$  manifold averaged over the (two almost degenerate)  $\Lambda$ -doublet states for the  $4_{04}$  and  $4_{14}$  levels of water. The arrows indicate the rotational states where theory and experiment are normalized.

quantum states, i.e.,

$$P_{jl} \sim \sum_{jk\lambda} (2J+1)(2k+1)t_\lambda^2 \left| \sum_{j''\lambda''} C_{j''\lambda''}^{Jl p_i} t_{\lambda''} [J-\lambda|J_i\lambda''] (-1)^\lambda + p_i (-1)^{J+J_i} [J\lambda|J_i\lambda''] F_l(jk\lambda|j''\lambda'') \right|^2, \quad (2)$$

where we have defined

$$F_{1(2)}(jk\lambda|j''\lambda'') = [a_j C(\frac{1}{2}kj|\frac{1}{2}1\frac{1}{2}) + b_j C(\frac{1}{2}kj|\frac{1}{2}1\frac{3}{2})][\mu_+(k\lambda|j''\lambda'')_{(-)}^{(+)} (-1)^{k-j+1/2} \mu_-(k\lambda|j''\lambda'')], \quad (3)$$

$$F_{3(4)}(jk\lambda|j''\lambda'') = [a_j C(\frac{1}{2}kj|\frac{1}{2}1\frac{3}{2}) - b_j C(\frac{1}{2}kj|\frac{1}{2}1\frac{1}{2})][\mu_+(k\lambda|j''\lambda'')_{(+)}^{(-)} (-1)^{k-j+1/2} \mu_-(k\lambda|j''\lambda'')], \quad (4)$$

$$[J\lambda|J_i\lambda''] = \begin{pmatrix} J & 1 & J_i \\ \lambda & 1 & \lambda'' \end{pmatrix} \begin{pmatrix} J & 1 & j_i \\ \lambda & -1 & \lambda'' \end{pmatrix}, \quad (5)$$

$$\mu_\pm(k\lambda|j''\lambda'') = \int_0^\pi d\gamma \sin\gamma d_{\pm 1\lambda''}^k(\gamma) Y_{j''\lambda''}(\gamma, 0). \quad (6)$$

In Eq. (6)  $\gamma$  is the orientation angle between the intramolecular OH vector and  $\mathbf{R}$ , the vector between the molecular center-of-mass and the H atom. In Eq. (2)  $J_i$  is the initial total angular momentum,  $p_i$  determines the parity of the  $\text{H}_2\text{O}$  (nuclear) ground-state wave function, and  $t_\lambda = \frac{1}{2}$  for  $\lambda=0$  and  $t_\lambda = 1/\sqrt{2}$  otherwise. The coefficients  $a_j$  and  $b_j$  are defined by<sup>9</sup>

$$a_j = \left[ \frac{X - |\tilde{\lambda} - 2|}{4X} \right]^{1/2}, \quad b_j = \left[ \frac{X + |\tilde{\lambda} - 2|}{4X} \right]^{1/2}, \quad (7)$$

$$X = [4(j + \frac{1}{2})^2 + \tilde{\lambda}(\tilde{\lambda} - 4)]^{1/2}, \quad (8)$$

with  $\tilde{\lambda} = -7.5$  for OH.  $l=1$  (3) and  $l=2$  (4) denote the lower (upper)  $\Lambda$ -doublet states of  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$ , respectively. The vibrational degrees of freedom are neglected for both  $\text{H}_2\text{O}$  and OH, because we have found in test calculations that rotational and vibrational degrees of freedom are to a large extent separable.  $C(\cdots|\cdots)$ ,  $(\cdots)$ ,  $d_{mm}^k$ , and  $Y_{jm}$  are Clebsch-Gordan coefficients,  $3j$  symbols, rotation matrices, and spherical harmonics, respectively.

The coefficients  $C_{j''\lambda''}$  are the expansion coefficients of the ground-state wave function in terms of parity-adapted angular basis functions.<sup>10</sup> They are obtained numerically in a completely variational procedure for each rotational state of  $\text{H}_2\text{O}$  separately using the Sorbie-Murell<sup>11</sup> potential-energy surface.<sup>12</sup> Details of these calculations will be given in a future paper. The expansion coefficients are in principle  $R$  dependent; however, here we take only their relative values at  $R = 1 \text{ \AA}$  (the equilibrium separation) because the radial and the angular parts of  $\Psi_{\text{g.s.}}$  are approximately separable. Furthermore, we assumed that the component of the transition dipole function perpendicular to the  $\text{H}_2\text{O}$  plane is independent of the spatial coordinates. In conclusion, all the information about the initial state of  $\text{H}_2\text{O}$  is contained in the coefficients  $C_{j''\lambda''}$  while the population of the fine-structure states of OH

is determined by the  $F_l$  of Eqs. (3) and (4).

This theory is applied to the photodissociation of  $\text{H}_2\text{O}$  out of the  $J_i = 4$  rotationally excited states. The agreement with the experimental results (normalized to theory separately for each rotational  $\text{H}_2\text{O}$  state) is surprisingly good. The oscillatory structure of the rotational distributions in Fig. 1 is reproduced for all the different projection quantum numbers, probably within experimental error. The remaining small discrepancies might vanish, if the final-state interaction were taken into account. The differences between the various initial states are solely induced by the initial wave function. The oscillatory structure is primarily due to the behavior of the coefficients  $C_{j''\lambda''}$ , but also to the phase factor  $(-1)^{k-j+1/2}$  in Eqs. (3) and (4), which changes sign as  $j$  is increased by one. The special form of the functions  $F_l$  predicts that the rotational distributions for the lower ( $l=1$  or 3) and the upper ( $l=2$  or 4)  $\Lambda$ -doublet states for  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$ , respectively, are out of phase as demonstrated for the  $4_{14}$  level in Fig. 2. As a consequence, the  $\Lambda$ -doublet averaged distributions are much smoother as shown in Fig. 3 for the  $4_{04}$  and  $4_{14}$  levels.

Through comparison of  $F_1$  with  $F_3$  (or  $F_2$  with  $F_4$ ), Eq. (2) predicts that the rotational distributions for  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  are out of phase with respect to  $j$ , or in phase with respect to  $N$  ( $N = j - \frac{1}{2}$  for  $^2\Pi_{3/2}$  and  $j + \frac{1}{2}$  for  $^2\Pi_{1/2}$ ) as actually found in the experiment. Furthermore, the experimental ratio  $^2\Pi_{1/2}:^2\Pi_{3/2} \approx N:(N+1)$  is also approximately reproduced by the calculations. Finally, the ratio between the populations of the two  $\Lambda$  doublets (for a given multiplet state) is reproduced in qualitative agreement with the experiment. This is demonstrated in Fig. 2, where theory and experiment are normalized only for the lower  $\Lambda$  doublet and the same normalization factor is used for the upper  $\Lambda$  doublet.

The good agreement of experimental results and theoretical predictions underlines the power of the present simple theory. *The comparison is quantitative on the basis of six quantum numbers, three specifying the initial state of  $H_2O$  and three specifying the final state of  $OH$ .* In all cases where experimental data are available (a few are only shown here), the agreement is of similar quality. Thus we conclude that the product quantum-state distributions are completely understood for both the fine structure and the rotational levels. The cornerstones of the model are the assumption of weak inelastic effects (which has actually been checked on an *ab initio* basis<sup>7</sup>), the inclusion of the electronic states of  $OH(^2\Pi)$ <sup>8</sup>, and numerically exact wave functions for rotationally excited levels of  $H_2O$ .<sup>12</sup>

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