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Citation: The Journal of Chemical Physics **88**, 6255 (1988); doi: 10.1063/1.454464 View online: http://dx.doi.org/10.1063/1.454464 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/88/10?ver=pdfcov Published by the AIP Publishing

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Correlations between angular momenta of coincident product pairs

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(Received 22 December 1987; accepted 26 January 1988)

The correlation between angular momenta of the coincident product pairs formed in an elementary dissociation process has been investigated. Doppler shift measurements are used in connection with state-specific detection of scattered photofragments by laser-induced fluorescence. The method is demonstrated in the photodissociation of H_2O_2 and D_2O_2 at 193 and 266 nm where Doppler profiles of OH (OD) absorption lines are used to determine the (average) rotational energy of the OH (OD) partner molecule coincidently formed in the same elementary fragmentation process. At high product rotations the partner molecules are generated with comparable angular momenta, while at low rotational excitation a more complex correlation is observed. In addition to the partner fragment distribution, dissociation energies were determined to be 197 kJ/mol for HO–OH and 204 kJ/mol for DO–OD, which are significantly lower than the previously recommended values.

I. INTRODUCTION

The determination of directional quantities by Doppler spectroscopy in connection with laser-induced fluorescence has opened a new way in elucidating the dynamics of chemical events.^{1,2} While time-of-flight measurements combined with mass spectroscopic detection³ determines the correlation between the transition dipole moment μ of the parent molecule and the recoil velocity v of the fragment, i.e., the product angular distribution, Doppler spectroscopy, in addition, is an excellent tool in measuring the correlation between μ and the total angular momentum of the product J and, especially, the correlation between v and J.⁴⁻⁹ Since the $\langle \mathbf{v} \cdot \mathbf{J} \rangle$ correlation is related to the repulsive force exerted in the fragmentation process, a characterization of the parent geometry and its potential energy surface in the excited state is feasible. If more than one upper electronic state is responsible for the fragmentation process, then the contribution of each single dissociation channel to the overall mechanism can be determined by knowledge of the vector correlations between μ , v, and J, provided the direction of each transition dipole moment is known or can be extracted from the same experiment.7 Further information about molecular correlations can be obtained by measuring the population of spinorbit¹⁰ and Λ doublet states¹¹ as a function of product rotation.

Although our understanding about dissociation processes has increased significantly by the determination of directional properties, an extremely important correlation in molecular reaction dynamics remains still unknown: The correlation between the rotational angular momenta (N_A, N_B) of the molecular products A and B formed in the same elementary process¹²

$$AB + h\nu \to A(N_A) + B(N_B). \tag{1}$$

This corresponds to a measure of the state-selected microscopic reaction probabilities $P(N_A, N_B)$ for formation of coincident product pairs A + B in the rotational states N_A and N_B . The only attempt to determine $P(N_A, N_B)$ has been carried out by application of information theory where the summation over N_A or N_B yielded optimal agreement with the experimentally obtained product state distributions $P(N_A)$ or $P(N_B)$, respectively.¹³

The present paper reports on a primary investigation of coincident product pair formation in the photodissociation of hydrogen peroxide and its deuterated analog at 193 and 266 nm in bulk and beam experiments. Both hydroxyl products originating from the same parent molecule are chemically identical. However, there is, *a priori*, no reason that their rotational energy generated in the *same* dissociation process has to be equivalent. Only the probability matrix $P(N_A, N_B)$ is symmetric, $P(N_A, N_B) = P(N_B, N_A)$, and consequently, the product state distribution of both fragments is identical, $P(N_A) = P(N_B)$.

In addition to the partner fragment distribution, the dissociation energy is determined by knowledge of the entire energetics in the fragmentation process of hydrogen peroxide and its deuterated analog.

II. MEASUREMENT OF COINCIDENT PRODUCT PAIRS

The internal state distributions of nascent OR (R = H,D) products have been probed under collision-free conditions in beam and bulk experiments using LIF as diagnostic tool. Details of the experimental setup have been described elsewhere.^{2,7} In short, a photolysis laser (ArF excimer laser at 193 nm or frequency quadrupled Nd:YAG laser at 266 nm) and the probing dye laser beams are polarized and counterpropagating or in mutual orthogonal geometry. Undispersed total fluorescence light is detected perpendicular to both beams.

Doppler profile measurements have been carried out to obtain information about directional properties involved in the dissociation process and, especially, to determine product recoil velocities. If the fragments are formed with a single velocity v and if polarization effects in detection are negligible, then the intensity of each spectral line as a function of

0021-9606/88/106255-05\$02.10

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frequency is given by [cf. Eq. (14) in Ref. 2]

$$I(\nu) = C \frac{P(i)}{2\Delta\nu_D} \left[1 + \beta_{\text{eff}} P_2(\cos\theta) P_2\left(\frac{\nu - \nu_0}{\Delta\nu_D}\right) \right]$$

for $|\nu - \nu_0| \leq \Delta\nu_D$, (2)

where P(i) represents the formation probability of the observed fragment A in state $|i\rangle$. θ describes the angle between the E vector of the dissociating laser light and the direction of the analyzing laser beam $P_2(x) = (3x^2 - 1)/2$ is the second Legendre polynominal, and the maximum Doppler shift Δv_D is given by $\Delta v_D = v_0(v/c)$. The anisotropy parameter $\beta_{\rm eff}$ contains the information on the vector correlations between the transition dipole moment of the parent and the rotational and translational motion of the product. When the fragments are formed in the same state $|i\rangle$ but with dif*ferent* velocities v_k , then the line shape is given by a sum of profiles described by Eq. (2). The fit of such a function to the recorded Doppler line shape yields, in principle, the fragment velocities v_k , provided the bandwidth of the analyzing dye laser is sufficiently small, and the anisotropy parameters $\beta_{\rm eff}$ are close to zero. In the case of one photon UV dissociatin of R_2O_2 (R = H, D) the fragments are generated with low internal excitation which results in a very narrow recoil velocity distribution.^{2,6,7,14-18} Therefore, only the wings of an OR Doppler profile are influenced by the different fragment velocities, while the center of the line is mainly determined by the anisotropy parameter β_{eff} . Hence, the velocity distribution can also be measured for an anisotropic fragmentation process. If necessary, the influence of β_{eff} on the Doppler profile can be eliminated by using an experimental configuration with the "magic" observation angle $\theta_m = 54.7^\circ [P_2(\cos \theta_m) = 0]$. This is a consequence of the cylindrical geometry determined by the experimental conditions. Observation of the ensemble of ejected products at θ_m will result in a sum of rectangular Doppler profiles.

Since the fragmentation process is subject to several constraints, further limitations on the recoil velocities v_k have to be considered. Conservation of energy demands that the available energy E_{av} ,

$$E_{\rm av} = h\nu + E_{\rm in} - E_D, \tag{3}$$

which is determined by the photon energy hv, the dissociation energy E_D , and the internal energy E_{in} of the parent molecule, has to be transferred into translational and internal energy of both products. Since photodissociation of R_2O_2 at 266 and 193 nm generates OR product molecules without vibrational excitation, only the rotational energies of the fragments have to be considered:

$$E_{\rm av} = E_{\rm rot}(A) + E_{\rm rot}(B) + \frac{1}{2}m_A v_A^2 + \frac{1}{2}m_B v_B^2. \tag{4}$$

The total linear momentum has to be zero in the center of mass systems, $\mathbf{p}_t = \mathbf{p}_A + \mathbf{p}_B = 0$. Hence, a further condition between E_{rot} and v_A is given by

$$E_{\rm rot}(B) = E_{\rm av} - E_{\rm rot}(A) - m_{\rm OR} v_A^2,$$
 (5)

with $m_{OR} = m_A = m_B$ and $v_A = v_B$. The velocity v_A reflects the internal energy of the partner product B and can be measured very accurately by Doppler spectroscopy using a dye laser with sufficient resolution. Furthermore, the rotational energy $E_{rot}(A)$ of the product OR_A is well known from the term value of the initial level assigned by LIF spectroscopy. For a fixed value of E_{av} the rotational energy $E_{rot}(B)$ of the *partner* product formed in the *same* dissociation process can be determined using Eq. (5). Therefore, an accurate measurement of the recoil velocities v_k , which are related to the maximum Doppler shifts $\Delta v_D(k)$ in Eq. (2), of single lines allows a determination of the product state distributions of the partner molecules formed in the same fragmentation processes. Precise Doppler profile measurements of all transitions which probe different internal energies of one of the products reflect the complete microscopic reaction probability $P(N_A, N_B)$.

To resolve the complete rotational state distribution of OH product pairs, the uncertainty of the available energy has to be sufficiently small, and the bandwidth of the analyzing dye laser has to be of the order

$$\delta v_1 \leq |\Delta v_D(k) - \Delta v_D(k+1)|, \tag{6}$$

where k and k + 1 label consecutive rotational states of the coincidently formed partner molecule OH_B .

III. RESULTS AND DISCUSSION

In the present experiments we have to consider the limited resolution of the applied dye laser and the internal energy of the parent molecule at room temperature. In total, both effects correspond to an effective bandwidth of $0.12 \text{ cm}^{-1,7}$ which is according to Eq. (6) not small enough to obtain the detailed joint reaction probability $P(N_A, N_B)$. However, for a specific rotational state N_A , corresponding to the rotational energy $E_{\text{rot}}(\text{OH}_A)$ of an OH_A product, the mean rotational state $\langle N_B \rangle$ [or mean rotational energy $\langle E_{\text{rot}}(\text{OH}_B) \rangle$] of the coincidently formed OH_B fragment can be determined.

The recorded Doppler profiles were fitted to Eq. (2) with suitable convolution of the laser bandwidth and R_2O_2 parent molecule motion. As an example, the measured mean Doppler width Δv_D is plotted in Fig. 1 as a function of the rotational energy $E_{rot}(OR_A)$ of OH (triangles) and OD (squares) fragments generated in the 266 nm photolysis of room temperature parent peroxides. The correlation



FIG. 1. Measured Doppler width as a function of the rotational energy of the OH (triangles) and OD (squares) fragment generated in the photolysis of *thermal* (T = 300 K) H₂O₂ and D₂O₂ at 266 nm. The Doppler width function (solid line) is used to calculate the mean rotational energy of the partner molecule formed in the same dissociation process.



FIG. 2. Correlation between angular momenta of the coincident OR product pairs $OR_A + OR_B(R = H,D)$ formed in the photodissociation of *thermal* R_2O_2 at 266 nm. The abscissa represents a specific rotational state N_A of an OR_A product while the mean rotational state $\langle N_B \rangle$ of the other coincidently formed OR fragment is represented by the ordinate. The bisecting line labels the special case where both partner fragments are formed with the same rotation, $\langle N_B \rangle = N_A$.

between observed Doppler width and OR_A rotational energy is significant within experimental resolution. We may accept a smooth function for the dependence of Δv_D on E_{rot} (OR_A) because it is unlikely that the inherent dissociation mechanism changes dramatically between consecutive rotational states. Therefore, it is feasible to fit the Δv_D values to a polynomial of second order to reduce the influence of any scattering in the data on the determination of the mean rotational energy $\langle E_{rot} (OR_B) \rangle$ of the partner product OR_B . The evaluated Doppler width function is used to calculate $\langle E_{rot} (OR_B) \rangle$ according to Eq. (5).

Figure 2 shows the correlation between the rotation of the partner fragments in the 266 nm photodissociation of H_2O_2 (triangles) and D_2O_2 (squares). With increasing E_{rot} (OR_A) the mean rotational energy $\langle E_{rot}$ (OR_B) \rangle of the partner product OR_B is also enlarged. Fragments generated in low rotational quantum states have (on the average) partner molecules with rather low rotational excitation, and



FIG. 3. Correlation between angular momenta of OH_A and OH_B product pairs formed in the photodissociation of *thermal* H_2O_2 at 193 nm. The abscissa represents a specific rotational state N_A of an OH_A product while the mean rotational state $\langle N_B \rangle$ of the other coincidently formed OR fragment is represented by the ordinate.



FIG. 4. Correlation between angular momenta of OH_A and OH_B product pairs formed in the photodissociation of *jet-cooled* H₂O₂ at 193 nm.

fragments created in high rotational states appear with partners in rather high rotational states. However, the strong correlation $|N_A| = |N_B|$ is not fulfilled as it is indicated in Fig. 2 by the systematic deviation of the data points from the bisecting line.

When room temperature hydrogen peroxide is excited at 193 nm, a partner product distribution is observed (see Fig. 3) which is comparable to that obtained at the photolysis wavelength of 266 nm. However, excitation of cold H_2O_2 parent molecules at 193 nm (see Fig. 4) leads to a more pronounced partner distribution. For higher rotational states ($N \ge 10$) the partner molecules are formed with nearly equivalent rotation

$$|\mathbf{N}_A| \simeq |\mathbf{N}_B|,\tag{7}$$

indicating a strong correlation between the two rotational vectors of the products $OH_A + OH_B$. The partner molecules of species generated at low rotational states are formed in a rotational state significantly higher than expected according to Eq. (7).

The result of comparable product partner rotation is supported by measurements of the vector correlation between the translational and rotational motion of the fragment. At the photolysis wavelength of 193 nm a very strong positive correlation is observed, indicating a preferentially parallel alignment of v and N.⁷ Such an alignment is only possible when the OH radicals are formed via torsional motion of the OH rotors during fragmentation. Performing this motion the rotational energy of the fragments OH_A and OH_B has to be the same, and the rotational vectors point into opposite directions, N_A = $-N_B$, due to conservation of angular momentum.

At low rotational states the correlation between v and N is found to decrease. A negative correlation corresponds to a preferentially perpendicular alignment between N and v. Such an alignment occurs when the rotation of the OH product originates from symmetric and antisymmetric bending motion of the OR rotor during fragmentation. For this type of motion, conservation of angular momentum can always be fulfilled for arbitrary N_A and N_B by the orbital angular momentum L_{AB} , even for cold parent molecules, where $N_{total} = N_A + N_B + L_{AB} \simeq 0$. Therefore, deviations from the strict relation expressed by Eq. (7) are possible. In Fig. 4,

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the representation of observed product pairs demonstrates that for rotational states $N_A < 10$ of the fragment OH_A the mean rotational state of the partner molecule OH_B is at a higher value. Therefore, the coincident pairs are no longer formed with the same angular momentum. In the lowest populated rotational level the partner fragment can only be generated in the same or in a higher rotational state. Hence, it is not surprising that the mean rotation of the product OH_B is higher than the rotation of the partner molecule OH_A .

Product rotation is determined by the potential energy surfaces involved in the dissociation process. However, a further influence on the fragment motion may result from initial excitation of the parent. The internal parent motion, i.e., vibration and rotation, is responsible for the different partner distributions observed in the photodissociation of thermal (Fig. 3) and jet cooled (Fig. 4) hydrogen peroxide. Parent translational motion can be neglected, since the fragments are observed in the center of mass system. From the six vibrational modes in H_2O_2 only the v_4 torsional mode is excited at room temperature.² Parent rotation may also be transferred into product rotation. However, only rotation about the O-O internuclear axis can significantly influence fragment rotation, because any rotation perpendicular to this axis will mainly pass over to fragment velocity and orbital angular momentum, due to the mass distribution in the peroxide C_2 ground state geometry. Only rotation about the O-O axis and excitation of the v_4 torsional mode will therefore contribute significantly to the rotational motion of the product pairs. Both motions will align the rotational vector N_{P} induced by the motion of thermal $H_{2}O_{2}$ along the O-O internuclear axis, which is the direction of separation.

The observed final rotation of the OH fragment is dependent on the alignment between N(OH), the OH rotational vector induced in the dissociation process, and N_p. We have to distinguish between OH rotation generated by a bending-like motion and product rotation induced by a torsional motion of the OH rotors. In the former case the rotations of the partners can be different, $N(OH_A) \neq N(OH_B)$, but have to be perpendicular to the direction of separation $[N(OH_A),N(OH_B)\perp O-O]$. In the latter case both partners exhibit the same absolute value of rotation, $N(OH_A)$ $= N(OH_B) = N(OH)$, and are aligned parallel to the recoil direction, N(OH) ||O-O.

For product rotation induced by *torsional* motion [N(OH)||O-O] and influenced by parent rotation (N_P) about the O-O internuclear axis, the final OH partner molecule rotations, $N_f(OH_A)$ and $N_f(OH_B)$, are given either by $N_f(OH_A) = N(OH) - N_P$ and $N_f(OH_B) = N(OH) + N_P$ or by $N_f(OH_A) = N(OH) + N_P$ and $N_f(OH_B) = N(OH) - N_P$. In any case the difference in rotation between both partner molecules is $\Delta N_{AB} = 2N_P$. For thermal H_2O_2 a mean parent rotation of $N_P \simeq 3\hbar$ can be extracted:

$$E_{\rm rot} = B_{\rm O-O} N_P (N_P + 1) = \frac{1}{2} kT, \tag{8}$$

where B_{O-O} is the H₂O₂ rotational constant around the O–O axis.¹⁹ Therefore, the fragmentation of rotationally excited parent molecules proceeding via torsional motion of the OH

rotors will generate partner molecule distributions with one of the fragments formed in a higher rotational state while the partner is created in a lower rotational state and vice versa.

Dissociation of torsionally excited H_2O_2 will result in final OH partner molecule rotations where N_p has either to be added to the OH rotation, $N_f(OH_A) = N(OH) + N_P$, $N_f(OH_B) = N(OH) + N_P$, or subtracted from OH rotation, $N_f(OH_A) = N(OH) - N_P$, $N_f(OH_B) = N(OH)$ $- N_P$. In any case no difference in rotation between both partner molecules is possible, $\Delta N_{AB} = 0$.

For product rotation induced via a *bending*-like motion of the OH rotor $[N(OH_A),N(OH_B)\perp O-O]$ the final OH partner molecule rotation is influenced only to a minor extent by parent motion, i.e., rotation about the O-O axis or excitation of the v_4 torsional mode. If the partner products are generated with the same rotation, $N(OH_A) = N(OH_B)$, then no difference in rotation between both partner molecules is expected, $\Delta N_{AB} = 0$. For $N(OH_A) \neq N(OH_B)$ the parent motion will slightly reduce any difference between the rotational motions of the partner products.

In summary, product pair rotation generated via torsional motion of the OH rotor during fragmentation is strongly effected by parent rotation resulting in a disturbance of the former strong correlation between $N(OH_A)$ and $N(OH_B)$. On the other hand, partner rotation induced via a bending-like motion of the OH rotor will only be influenced to a minor extent by the initial parent motion, with the tendency of $N(OH_A)$ and $N(OH_B)$ becoming more comparable.

In the photolysis of H_2O_2 at 193 nm, we determined the expectation values of the squared angular momentum components to be $\langle N_{\text{torsion}}^2 \rangle / N(N+1) \simeq 0.81$ for hydrogen peroxide at room temperature and $\langle N_{\text{torsion}}^2 \rangle / N(N+1) \simeq 0.70$ for jet cooled H_2O_2 .⁷ Therefore, most of the product rotation originates from the torque provided by the strong torsional angular dependence of the upper state potential [N(OH) || O-O]. Thus, in the photolysis of thermal peroxide the partner molecule of a fragment observed in a high rotational state will be found in a significantly lower state. For example, hydroxyl radicals observed at $N(OH_A) = 18$ will have partners around $N(OH_B) = N(OH_A) - 2N_P \simeq 12$.

At longer photolysis wavelengths the absorption cross section of R_2O_2 decreases strongly,²⁰ and extremely accurate Doppler width measurements were not carried out in a molecular beam photolysis experiment. However, bulk measurements were performed at the excitation wavelength of 266 nm with an accuracy comparable to the dissociation experiment at 193 nm. At the long wavelength edge of the R_2O_2 absorption spectrum a significant amount of product from rotation is generated bending motions. $\langle N_{\text{bend}}^2 \rangle / N(N+1) \simeq 0.5$ for $D_2 O_2^8$ and $\langle N_{\text{bend}}^2 \rangle / N(N+1) \simeq 0.5$ $N(N+1) \simeq 0.4$ for H₂O₂.² Therefore, we do not expect a pronounced influence of initial parent motion on the product pair distribution as it is observed in the photolysis at 193 nm. Especially the OD partner distribution should reflect more directly the pure fragmentation pattern. The partner molecules of such fragments generated at low rotation are formed at higher rotational states, while highly rotating hy-

TABLE I. Comparison between spectroscopic and thermodynamical data for the dissociation energy E_D of $\mathbf{R}_2\mathbf{O}_2$ (at T = 0 K) which is necessary to form two OR radicals in their lowest quantum state. The experimental error range is ± 3 kJ/mol, units are kJ/mol.

Condition	on E_D (HO–OH) E_D (DO–OD) Comment		
193 nm, bulk	199		Doppler spectr.
193 nm, beam	197	•••	Doppler spectr.
266 nm, bulk	194	204	Doppler spectr.
	207	211	thermodynamic (Ref. 21)

droxyl radicals have partners which are generated with nearly the same rotation $N_A \simeq N_B$ indicating again a distinct correlation between the two rotational vectors of the products $OR_A + OR_B$.

We have demonstrated a new method for a direct experimental determination of joint microscopic reaction probabilities for two products emerging from the same chemical event. The complete probability matrix $P(N_A, N_B)$ was not accessible in the present experiment due to limited laser resolution. However, $P(N_A, N_B)$ can be obtained by using a laser system with a sufficiently small bandwidth, e.g., a cw dye laser in combination with a pulsed amplifier. Such a laser system is used in a current experiment to obtain individual correlations between the angular momenta of both OH fragments in the photodissociation of hydrogen peroxide.

Finally, the complete analysis of the energetics involved in a dissociation process allows a spectroscopic determination of the dissociation energy E_D . Using Eqs. (3) + (5) one obtains for the present experiment

$$E_{D} = hv_{P} + E_{int} \left(\mathbf{R}_{2} \mathbf{O}_{2} \right) - \sum_{k} P(k) \left[2E_{rot} \left(k \right) + m_{OR} v_{k}^{2} \right],$$
(9)

where P(k) represents the probability of observing a product with the rotational energy $E_{\rm rot}(k)$. In Table I the spectroscopically evaluated dissociation energies are shown in comparison to thermodynamical data. All values of E_D obtained by Doppler spectroscopy are about 5% lower than already published ones.²¹ The only systematic error in our determination of the dissociation energies might result from translational relaxation processes. However, these effects would reduce the measured Doppler widths and hence, the calculated energies E_D would rather increase than decrease. Therefore, we recommend a value of $E_D(HO-OH)$ = (197 ± 3) kJ/mol for the dissociation of H₂O₂ into two OH radicals in their lowest quantum states and E_D (DO-OD) = (204 ± 3) kJ/mol for the deuterated analog.

ACKNOWLEDGMENT

This work has been performed as part of a program of the Deutsche Forschungsgemeinschaft, whose financial support is gratefully acknowledged.

- ¹J. P. Simons, J. Phys. Chem. **91**, 5378 (1987); P. L. Houston, *ibid.* **91**, 5388 (1987).
- ²K.-H. Gericke, S. Klee, F. J. Comes, and R. N. Dixon, J. Chem. Phys. 85, 4463 (1986).
- ³R. B. Bernstein, *Chemical Dynamics via Molecular Beam and Laser Tech*nique (Oxford University, New York, 1982).
- ⁴R. N. Dixon, J. Chem. Phys. 85, 1866 (1986).
- ⁵G. E. Hall, N. Sivakumar, R. Ogorzalek, G. Chawla, H.-P. Haerri, P. L. Houston, I. Burak, and J. W. Hepburn, Faraday Discuss. Chem. Soc. 82, 13 (1987); G. E. Hall, N. Sivakumar, P. L. Houston, and I. Burak, Phys. Rev. Lett. 56, 1671 (1986).
- ⁶M. P. Docker, A. Hodgson, and J. P. Simons, Chem. Phys. Lett. **128**, 264 (1986); Faraday Discuss. Chem. Soc. **82**, 25 (1987).
- ⁷A. U. Grunewald, K.-H. Gericke, and F. J. Comes, Chem. Phys. Lett. **132**, 121 (1986); J. Chem. Phys. **87**, 5709 (1987); F. J. Comes, K.-H. Gericke, A. U. Grunewald, and S. Klee, Ber. Bunsenges. Phys. Chem. **92**, 273 (1988).
- ⁸S. Klee, K.-H. Gericke, and F. J. Comes, Ber. Bunsenges. Phys. Chem. **92**, 429 (1988).
- ⁹M. Dubs, U. Brühlmann, and J. R. Huber, J. Chem. Phys. 84, 3106 (1986); 86, 1249 (1987).
- ¹⁰I. Nadler, D. Mahgerefteh, H. Reisler, and C. Wittig, J. Chem. Phys. 82, 3885 (1985); I. Nadler, H. Reisler, and C. Wittig, Chem. Phys. Lett. 103, 451 (1984); F. Shokoohi, S. Hay, and C. Wittig, *ibid.* 110, 1 (1984); H Joswig, M. A. O'Halloran, R. N. Zare, and M. S. Child, Faraday Discuss. Chem. Soc. 82, 79 (1987).
- ¹¹A. M. Quinton and J. P. Simons, Chem. Phys. Lett. 81, 214 (1981).
- ¹²Rotational states are characterized by their nuclear rotational quantum number N instead of the total angular momentum quantum number J. Both descriptions are equivalent, since no spin selectivity is observed in the photofragmentation of R_2O_2 .
- ¹³F. J. Comes, K.-H. Gericke, and J. Manz, J. Chem. Phys. 75, 2853 (1981).
- ¹⁴G. Ondrey, N. van Veen, and R. Bersohn, J. Chem. Phys. 78, 3732 (1983).
- ¹⁵A. Jacobs, K. Kleinermanns, H. Kuge, and J. Wolfrum, J. Chem. Phys. 79, 3162 (1983); A. Jacobs, M. Wahl, R. Weller, and J. Wolfrum, Appl. Phys. B 42, 173 (1987).
- ¹⁶S. Klee, K.-H. Gericke, and F. J. Comes, J. Chem. Phys. 85, 40 (1986).
 ¹⁷K.-H. Gericke, S. Klee, and F. J. Comes, Chem. Phys. Lett. 137, 510 (1987).
- ¹⁸T. M. Ticich, M. D. Likar, H.-R. Dübal, L. J. Butler, and F. F. Crim, J. Chem. Phys. 87, 5820 (1987).
- ¹⁹H₂O₂ rotational constants were calculated from the moments of inertia published by A. Khachkuruzov and I. N. Przhevalskii, Opt. Spectrosc. 36, 172 (1974).
- ²⁰L. T. Molina and M. J. Molina, J. Photochem. 15, 97 (1981).
- ²¹Dissociation energy of H_2O_2 was taken from H. Okabe, *Photochemistry of Small Molecules* (Wiley, New York, 1978), p. 282, and D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data 9, 295 (1980). Dissociation energy of D_2O_2 was calculated comparing the values for the vibrational frequencies of H_2O_2 and D_2O_2 and the zero-point energies of OH and OD, see Ref. 17.