

Doppler spectroscopy of OH in the photodissociation of hydrogen peroxide

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The photofragmentation of hydrogen peroxide has been investigated at an excitation wavelength of 266 nm using polarized laser beams. Doppler spectroscopy in connection with the laser induced fluorescence technique was applied to determine the nascent translational distribution of OH products. The hydroxyl radicals are formed in their electronic ground state, $X^2\Pi_{3/2,1/2}$. The released energy is transformed almost exclusively in translation of these photoproducts. The $Q_1(4)$ transition in $\text{OH}(X^2\Pi_{3/2} \rightarrow A^2\Sigma^+)$ was used to study the anisotropic angular distribution of recoiling OH photofragments and analyzed to obtain information about the lifetime and symmetry of the excited dissociative state. The Doppler profiles for different directions of the electric field vectors of dissociation and probe laser relative to the detector axis have been determined for two different geometries. The angular distribution measured by Doppler spectroscopy, peaks in the direction perpendicular to the electric vector of the dissociating laser light, indicating that the predominant electronic excited state in H_2O_2 must be of 1A symmetry. An upper limit for the lifetime τ of the excited H_2O_2 parent molecule before dissociation is $\tau \leq 6 \times 10^{-14}$ s.

I. INTRODUCTION

Photodissociation of molecules is a primary chemical event and can be considered as the second half of a collision corresponding to a chemical reaction on the final electronic surface. The molecules can be optically prepared in a narrow distribution of the parent excited state and the outcome of the dissociative process can be analyzed in detail through, e.g., laser induced fluorescence (LIF), multiphoton ionization (MPI), or time-of-flight (TOF) experiments.¹

In terms of measurements concerning the kinetic energy and angular distribution of the ejected photofragments, the most frequently used technique is mass spectroscopy combined with TOF measurements. Laser induced fluorescence is the common method to measure the internal state distribution of the products, if these fragments are spectroscopically suitable. In addition, Doppler spectroscopy, applied in this work, can also be used to study the translation of the fragments (usually the domain of TOF) even in a bulk experiment. If the dissociating light is polarized, the fragments will not be distributed isotropically and the normalized angular distribution of products is given by

$$f(\theta) = [1 + \beta P_2(\cos \theta)]/4\pi, \quad (1)$$

where θ is the angle between the E vector of the dissociating light and the direction at which the fragment is detected.

In photodissociation experiments Doppler spectroscopy has been applied by Kinsey *et al.*² to study scattering processes. In the present work the method was used to investigate the photofragmentation of hydrogen peroxide at 266 nm. The products are two OH radicals both formed in the electronic ground state, $^2\Pi_{3/2,1/2}$. Hydrogen peroxide appears to be an excellent system for the study of photodissociation dynamics of polyatomic molecules, because both photofragments are molecules which can be probed *simultaneously* by the sensitive LIF technique; a well structured angular distribution can be expected because almost all

available energy appears in OH recoil and, in addition, the alignment of the OH fragment can also be determined using polarized laser beams.

Furthermore, the orientation of the transition moment in H_2O_2 will be obtained. In the following a short summary of the Doppler spectroscopy and the angular distribution in photodissociation is given. Then the experimental setup will be described and finally the obtained results will be discussed in relation to the anisotropic character of the fragmentation process.

II. ANGULAR DISTRIBUTION AND DOPPLER SPECTROSCOPY

For an electric dipole one photon transition the c.m. angular distribution $f(\theta)$ is given by Eq. (1), where $P_2(\cos \theta)$ is the second degree Legendre polynomial in $\cos \theta$:

$$P_2(\cos \theta) = [3 \cos^2 \theta - 1]/2. \quad (2)$$

The only experimental quantity which has to be determined is the anisotropy parameter β . Using reasonable models for the fragmentation process, this parameter β can give information on the symmetry, configuration, parent internal motion, and especially on the lifetime of the parent excited state. Thus, β plays a key role in understanding the photodissociation dynamics of molecules. This parameter has been analyzed by Zare and Herschbach,³ Bersohn and Lin,⁴ Jonah *et al.*,⁵ Bush and Wilson,⁶ and Yang and Bersohn.⁷

If a nonrotating molecule dissociates instantaneously after absorbing a photon, then the parameter β is given by the simple equation

$$\beta = 2P_2(\cos \gamma), \quad (3)$$

in which γ is the angle between the direction of dissociation and μ_{fi} , the transition dipole moment connecting the initial

state i with the final state f :

$$\mu_{fi} = \langle f | \mu | i \rangle. \quad (4)$$

For a diatomic molecule the direction of dissociation can only be the internuclear axis and consequently the angle γ can only be 0 or $\pi/2$, corresponding to a $\cos^2 \theta$ distribution [$f(\theta) = (3/8\pi)\cos^2 \theta; \beta = 2$] for a parallel transition, $\gamma = 0^\circ$, or a $\sin^2 \theta$ distribution [$f(\theta) = (3/8\pi)\sin^2 \theta; \beta = -1$] for a perpendicular transition, $\gamma = 90^\circ$.

Schmiel *et al.*⁸ have measured the parameter β for the dissociation of HI at 266 nm. They found both values $\beta = +2$ and $\beta = -1$, reflecting the two dissociation channels of HI in $\text{H} + \text{I}(^2P_{1/2})$ and $\text{H} + \text{I}(^2P_{3/2})$. For a polyatomic molecule the value of the angle γ is less restricted. Recoil at $\gamma = \arccos(3^{-1/2}) \cong 54.7^\circ$ would result in an isotropic distribution, because $\beta = 0$. But Doppler spectroscopy will still allow to determine the recoil velocity very accurate, as will be shown later.

So far, the influence of parent internal motion on the fragment angular distribution has not been taken into account. For a rotating or vibrating parent the parameter β is influenced by two further effects. First, the dissociation process may be slow with respect to the rotation during dissociation which means that the tangential velocity of the fragments during rotation can be compared with the recoil velocity and influences the velocity of the fragments. In the following we will call α the angle by which the recoil direction is deflected by the rotation of the parent molecule. Under these conditions, β is given by

$$\beta = 2P_2(\cos \gamma)P_2(\cos \alpha). \quad (5)$$

Secondly, if the dissociation is not instantaneous, β will be influenced by the ratio of the lifetime τ of the excited H_2O_2 to its rotational period.

Before fragmentation, the molecule will rotate through the angle $\delta = \omega\tau$, if ω describes the angular velocity and τ the lifetime of the parent in the excited state. Jonah *et al.*⁵ and Bush and Wilson⁶ have given classical and quantum mechanical derivations of the angular distribution; Yang and Bersohn⁷ have extended these derivations more systematically for arbitrary molecules. Following the work of Bush and Wilson, we find for a first order decay

$$\beta = 2P_2(\cos \gamma) [P_2(\cos \alpha) + \delta^2 - 3\delta \sin \alpha \cos \alpha] / [1 + 4\delta^2]. \quad (6)$$

For a prompt decay, $\tau \rightarrow 0$, the parameter β reduces to Eq. (5). For a long lifetime of the excited molecule in comparison with its angular velocity ($\tau \gg 1/\omega$), β is given by

$$\beta = P_2(\cos \gamma)/2. \quad (7)$$

The ejected photofragments are probed with narrow bandwidth lasers. In Doppler spectroscopy using LIF, the excitation frequency which will be "seen" by the product is given by

$$\nu = \nu_0 \left(1 \pm \frac{v}{c} \right), \quad (8)$$

where v is the projection of fragment velocity \mathbf{v}_f onto the direction of the probing laser beam. Kinsey² has given deri-

vations for the Doppler line shape and velocity distribution of the products. In the special situation of our experiment the θ dependence will give complete information on the photofragment angular distribution. This is because the fragment distribution is Π symmetric on the plane perpendicular to the electric field vector \mathbf{E} of the polarized dissociating light.

The corresponding photofragment Doppler profile for the center of mass fragment angular and velocity distribution $g(v_f)$ is then given by⁸

$$D(v, \theta) = \int_{|v|}^{\infty} \frac{1}{2v_f} [1 + \beta P_2(\cos \theta) P_2(v/v_f)] g(v_f) v_f^2 dv_f. \quad (9)$$

For a discussion of the experimental results the Doppler profiles have to be transformed from the center of mass to the laboratory frame. Our measurements were performed in a bulk experiment. Thus, this transformation is a "simple" convolution of the c.m. Doppler profiles with a Gaussian function which reflects the 300 K thermal translational (Doppler) distribution of H_2O_2 parent molecules.

III. EXPERIMENTAL

The experimental realization to analyze Doppler broadened line profiles was accomplished by the utilization of a fast photofragmentation-detection technique, where nascent OH radicals resulting from photodissociation of H_2O_2 were probed by laser induced fluorescence. The frequency quadrupled output of a Nd:YAG laser (Spectron, SL2Q) operating at a repetition rate of 12.5 Hz provided the 12 ns photolysis pulses. The typical pulse energy was about 12 mJ. The 266 nm radiation was weakly focused into the middle of a cubic aluminum chamber, passing a series of light baffles to reduce stray light from the entrance window. The absorption cross section of H_2O_2 was reported to be $3.86 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ at 265 nm.⁹

The second harmonic of the Nd:YAG laser pumped a frequency doubled dye laser (Lambda Physik, FL 2002 E, Rhodamin 101 in methanol) providing the required tunable laser pulses at 308 nm with an optical delay of 17 ns to excite the (0,0) band of the $\text{OH}(X^2\Pi_i \rightarrow A^2\Sigma^+)$ transition resonantly. The probe beam was used unfocused but collimated by baffles to a diameter of 3 mm. With an energy of less than 1 μJ per pulse and a pulse width of 10 ns probing of OH was found to be within the linear regime. The dye laser contained an intracavity étalon for narrowing the bandwidth, which was tuned by a computer-controlled stepping motor. The resulting linewidth was determined to be about 0.11 cm^{-1} by means of an external Fabry-Perot.

Each laser beam was linearly polarized, their planes of polarization could be rotated by $\lambda/2$ plates. Changes in photodissociation and probe beam polarization were performed under control of a Glan-Thompson prism. The applied laser beam arrangement permitted comparative experimentation at both the mutually orthogonal and the counterpropagated coaxially probed geometry.

The total undispersed fluorescence was viewed in a direction perpendicular to the laser beams with a photomultiplier (Hamamatsu, R 955, 1.2 kV) through a collection optics with all polarizations accepted equally. Scattered light

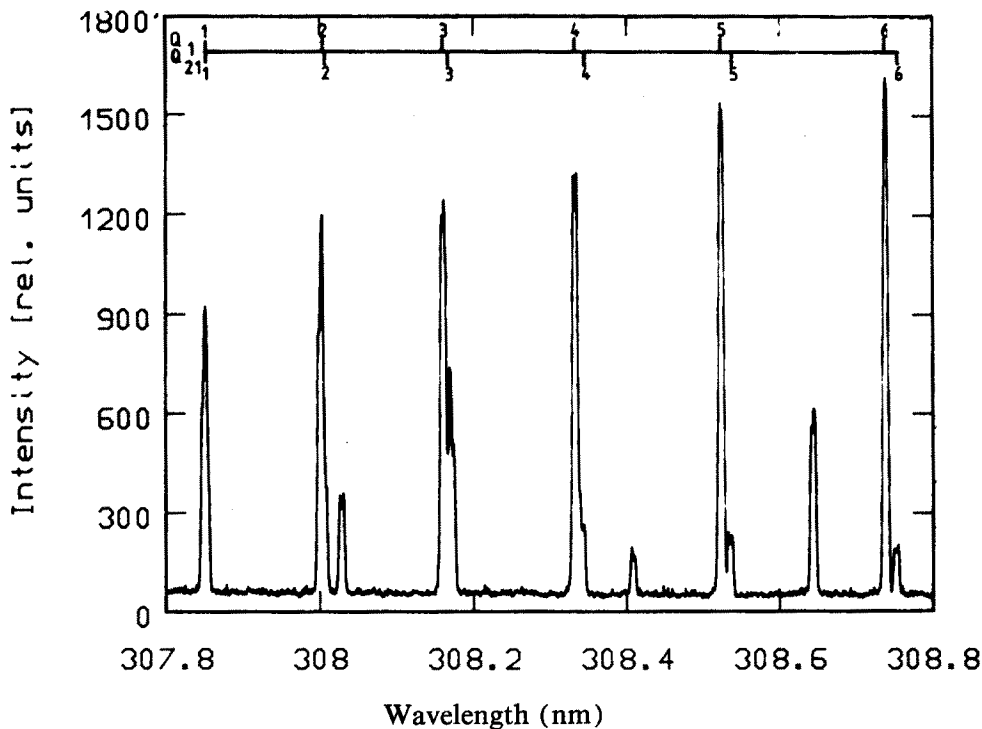


FIG. 1. Small section of the excitation spectrum of $\text{OH}(X^2\Pi)$ photofragments generated by the photolysis of H_2O_2 at 266 nm. The pump laser beam of the fourth harmonic of the Nd:YAG laser and the analyzing dye laser beam were counterpropagated and linearly polarized parallel to each other. Laser induced fluorescence was detected perpendicular to the propagation directions and to the E vector of the two laser beams. The photomultiplier accepted all polarizations equally. Experimental conditions were: $P_{\text{tot}} = 100$ mTorr, 17 ns time delay between photodissociating and analyzing pulse.

was reduced by a 310 nm interference filter (10 nm FWHM). For averaging and normalization to constant photolysis, respectively, probe laser output the signal was fed into a boxcar integrator (PAR 162 boxcar averager with the models 164/165 gated integrators) operating with a gate width of 500 ns.

Hydrogen peroxide (90%) was degassed prior to use and was allowed to flow through the chamber for some time to passivate the walls. A vacuum system permitted variations of the total vapor pressure in the probe cell in the range of 1 mTorr to 1 Torr. The typical pressure employed was 100 mTorr, which was sufficiently low to detect OH in its nascent state. It was kept constant within 5% during an experimental run controlled by a capacitance manometer (MKS Baratron). Continuous fast pumping through the chamber took care of the comparability of experimental conditions from one photolysis pulse to the other.

The detected OH absorption lines from dissociated H_2O_2 at 266 nm were assigned on the basis of the work of Dieke and Crosswhite.¹⁰ Figure 1 shows the Q_1 bandhead of the $A^2\Sigma^+ \leftarrow X^2\Pi_i(0,0)$ transition in low resolution of the rotational lines. From this the $Q_1(4)$ transition was chosen exemplary to analyze the variations of line shape with changes in photolysis and probe beam mutual geometry and polarization. For simplification of the fitting procedure concerning the β parameter the accompanying satellite $Q_{21}(4)$ was cut out computationally.

IV. RESULTS

Photodissociation of hydrogen peroxide in the ultraviolet spectral region leads to the production of OH radicals.^{11–13} At 193 and 248 nm the OH are generated in the electronic ground state.¹³ Below 172.2 nm, however, electronically excited OH are formed.¹¹ This also results if two photons at 193 nm are absorbed.¹² At 266 nm, as used in the

present experiment, no characteristic $\text{OH}(A^2\Sigma \rightarrow X^2\Pi)$ resonant transitions could be observed. Thus only one photon is absorbed by H_2O_2 and both OH radicals must be formed in their electronic ground state $^2\Pi_{3/2,1/2}$.

The Doppler profiles of the $Q_1(4)$ absorption line have been determined for different directions of the electric field vectors of both dissociation (E_d) and probe (E_a) lasers relative to the detector axis (z axis) for different geometries. The observed line profiles are influenced by different physical and experimental parameters: (a) the shape factor β representing the angular distribution; (b) the translational motion of the parent H_2O_2 ; (c) the velocity distribution $g(v_f)$ of OH product molecules; (d) the limited resolution of the probing dye laser system; and (e) background signals.

The translational motion of H_2O_2 as well as the limited spectral resolution of the measurement has been treated by folding the Doppler profile function [Eq. (9)] with the laser line profile and with the 300 K thermal Gaussian H_2O_2 distribution. For the laser line we have taken an additional Gaussian function with the experimentally determined laser linewidth of $\Delta\tilde{\nu} = 0.11 \text{ cm}^{-1}$ (FWHM) in the UV.

The width of the parent Gaussian distribution at frequency $\tilde{\nu}_0$ of the $\text{OH}(X^2\Pi, v' = 0) \rightarrow \text{OH}(A^2\Sigma, v' = 0)$ transition and at temperature $T = 300 \text{ K}$ is

$$\Delta\tilde{\nu} = \frac{\tilde{\nu}_0}{c} \left(\frac{8kT \ln 2}{m_{\text{H}_2\text{O}_2}} \right)^{1/2} = 0.069 \text{ cm}^{-1}. \quad (10)$$

The combination with the laser line gives the overall Gaussian convolution function with $\Delta\tilde{\nu}_1 = 0.13 \text{ cm}^{-1}$ (FWHM).

The velocity distribution $g(v_f)$ in the c.m. system is determined by the energies of this process. The available energy (E_{av}) which is given by the excitation wavelength, the internal energy of the parent H_2O_2 , $E_{\text{int}}(\text{H}_2\text{O}_2)$, and by the dissociation energy D_0 ,¹⁴

$$E_{\text{av}} = h\nu + E_{\text{int}}(\text{H}_2\text{O}_2) - D_0 = 246 \text{ kJ/mol} \quad (11)$$

has to be distributed among the kinetic (E_{kin}) and internal (E_{int}) energy of both OH products.

A broad excitation of internal degrees of freedom of OH photofragments will result in a broad velocity distribution of the products. On the opposite, a very narrow excitation or a minor internal excitation of OH radicals will give us a very narrow velocity distribution and the Doppler profile can be approximated by just one value for the velocity v_f . The nascent internal state distribution of OH ($X^2\Pi, v'', J''$) for rotational and vibrational levels as well as for both spin states and Λ levels was determined. Furthermore the alignment of OH angular momentum was measured. The influence of internal motion of the parent H_2O_2 molecule on the state distribution and alignment of the product has also been investigated in a supersonic jet. The results of these studies will be published in a forthcoming paper.¹⁵ The important result is that OH fragments are formed with very low internal excitation, e.g., no vibrationally excited hydroxyl radicals were found, and the available energy is transformed almost exclusively in translational energy of OH photoproducts.

Furthermore, in the title experiment we measured the translational energy by Doppler spectroscopy and, as will be shown later, the observed Doppler shift corresponds to a value of kinetic energy which is identical to the available energy within the experimental error.

Thus, the assumption of a very narrow velocity distribution $g(v_f)$ for the OH fragment is valid and the approximation of a single velocity can be used. Under these conditions and a detection geometry of $\theta = \pi/2$, Eq. (9) reduces to

$$D(v, v_0) \sim \left[1 + \frac{\beta}{4} - \frac{3}{4} \beta \left(\frac{v - v_0}{\Delta v_D} \right)^2 \right] \text{ for } |v - v_0| \leq \Delta v_D, \quad (12a)$$

where $\Delta v_D = v_0 v_f / c$ is the Doppler shift from line center v_0 . For a detection geometry of $\theta = 0$ we get

$$D(v, v_0) \sim \left[1 - \frac{\beta}{2} + \frac{3}{2} \beta \left(\frac{v - v_0}{\Delta v_D} \right)^2 \right] \text{ for } |v - v_0| \leq \Delta v_D. \quad (12b)$$

These profiles were convoluted by the Gaussian function

$$P(v, v_1) \sim \exp \left[-4 \ln 2 \left(\frac{v - v_1}{\Delta v_1} \right)^2 \right] \quad (13)$$

to consider parent translation and dye laser linewidth ($\Delta \tilde{\nu}_1 = 0.13 \text{ cm}^{-1}$ FWHM). A least square fit procedure then yields background, amplitude, Doppler shift, and the important anisotropy parameter β .

The observed Doppler profiles for the $Q_1(4)$ transition are shown in Fig. 2 together with the best fitted curve. Figure 2(a) represents the profiles which were measured at a detection geometry of $\theta = \pi/2$, while in Fig. 2(b) the detection geometry was $\theta = 0$. Although both profiles look completely different, the same β parameter, $\beta = -0.71 \pm 0.11$ was obtained. The value found for the Doppler shift is $\Delta \tilde{\nu}_D = (0.40 \pm 0.02) \text{ cm}^{-1}$. The characteristic Doppler split line shape which was found under coaxial geometry changed into a Gaussian profile after admitting 8 Torr argon to the cell as an effect of translational relaxation of OH. The observed linewidth was determined to be 0.19 cm^{-1} which leads to a width of 0.16 cm^{-1} after deconvolution (laser

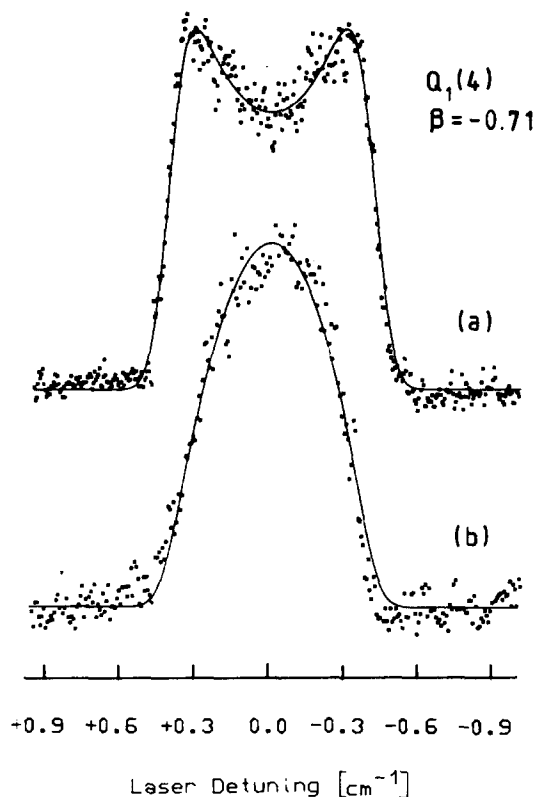


FIG. 2. High resolution excitation spectra in the region around the $Q_1(4)$ transition shown in Fig. 1. The $Q_{21}(4)$ satellite line was cut out computationally for simplification of fitting the experimental data at the line profiles described by Eq. (12) convoluted with a 300 K thermal motion of H_2O_2 and a Gaussian laser profile. In (a) the pump and probe laser beams were counterpropagated and polarized parallel to each other, whereas in (b) the propagation directions of the beams were mutually orthogonal still having the same polarizations as in the situation described in Figs. 1 and (a).

linewidth in the UV 0.11 cm^{-1}). At the present time Doppler profiles for different rotational states of OH ($^2\Pi_i$) and for different transitions [$^2\Pi(J'') \rightarrow ^2\Sigma(J' = J'' \pm 0, 1)$] as a function of the polarization of the exciting dye laser beam are being measured which will be discussed elsewhere in the light of the theory recently developed by Dixon.¹⁶

The theory of rotational anisotropy has been developed in different papers.¹⁷⁻¹⁹ In principle, the anisotropies of the translational and rotational motions of the *fragments* are correlated with the alignment of the *parent* molecule transition dipole. Thus the photoproduct rotational and translational motions should also be correlated with one another and the observed Doppler profiles of the recoiling OH products should also depend on the polarization of the analyzing dye laser beam. Indeed, we could determine such a dependence of the profiles for the first time. For an analysis of these findings, Eq. (9) has to be extended to higher order Legendre polynomials [$P_4(v/v_f)$, $P_6(v/v_f)$].²⁰ The results of this analysis in connection with the experimental observations will be published in a forthcoming paper.¹⁵

V. DISCUSSION

Figure 2(a) shows the observed Doppler profile under the experimental condition of both laser beams being polarized parallel to each other and counterpropagated. The an-

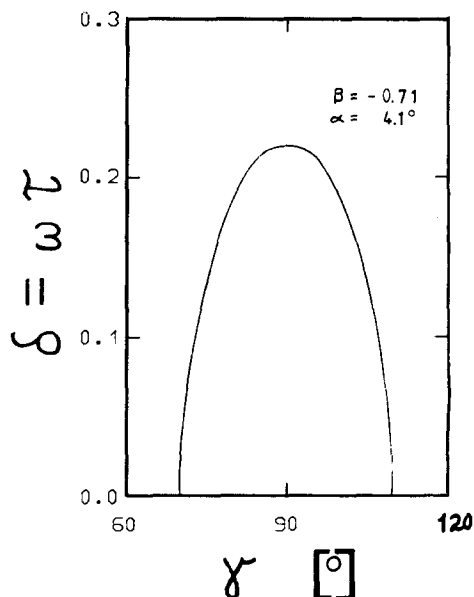


FIG. 3. Plot of rotation angle δ as a function of internal recoil angle γ . *A priori*, the values of γ and δ lie in the ranges $0 < \gamma < \pi$ and $0 < \delta < \infty$; with the experimental values of β and α , these ranges are limited [Eq. (6)] and the value of the internal recoil angle is about $90^\circ \pm 18^\circ$. For $\gamma = \pi/2$ the rotation angle $\delta = \omega\tau$ has its maximum value and the calculated lifetime $\tau = 60$ fs is an upper limit for the lifetime of H_2O_2 in the electronic excited state.

gular distribution of recoiling OH radicals from the dissociation at 266 nm peaks in a direction perpendicular to the polarized dissociating laser light. This proves that the predominant, if not exclusive, electronic excited state in H_2O_2 is of 1A symmetry. A positive value of the parameter β would indicate a 1B symmetry. Although only the OH photofragments were observed, we could gain information about the spectroscopy of the parent H_2O_2 molecule.

One important feature in this work is the large value of $\Delta\tilde{\nu}_D = (0.40 \pm 0.02) \text{ cm}^{-1}$ which corresponds to a translational energy of $E_{\text{kin}} = (240 \pm 25) \text{ kJ/mol}$ for both OH radicals. This value can be compared with the total available energy, $E_{\text{av}} = 246 \text{ kJ/mol}$. Hence, the products are formed with a very high amount of translational energy and our assumption of low internal excitation of the fragments is fulfilled.

With the result we obtained for the translational energy of OH products, we can estimate how the observed value of β is effected by H_2O_2 rotation. If the velocity of separation would be sufficiently low, the rotation of the molecule would substantially alter the asymptotic velocity. For the high amount of released translational energy, observed in the dissociation of H_2O_2 , the tangential velocity (v_t) of the fragments during rotation of the parent H_2O_2 is small compared to the axial velocity (v_0) of O–O recoil.

The tangential velocity of the OH product is $v_t = \omega d$; d is the distance from the center of mass of H_2O_2 to the center of mass of the OH fragment and ω being the angular velocity. Angular momentum is not conserved with respect to each molecular axis of H_2O_2 , but from the equipartition principle we conclude that there will be an average of $1/2 \text{ kT}$ for each

of the principal axes. From the relation

$$\frac{I\omega^2}{2} = \frac{kT}{2} \quad (14)$$

we get $\omega = 3.6 \times 10^{12} \text{ s}^{-1}$ and $v_t = 265 \text{ m s}^{-1}$.²¹ The recoil velocity, given by

$$v_f = c\Delta\nu_D/v_0, \quad (15)$$

was determined to be $v_f = (3700 \pm 200) \text{ m s}^{-1}$. This value is much larger than the tangential velocity and the angle α at which recoil occurs is

$$\alpha = \arcsin(v_t/v_f) \cong 4.1^\circ. \quad (16)$$

Using this value of α in Eq. (6) and our experimental value of $\beta = -0.71$, we get a graph of γ vs δ shown in Fig. 3. From this plot we can estimate an upper limit of the lifetime τ of the parent H_2O_2 molecule in the electronic excited state (which should be of 1A symmetry). The parameter $\delta = \omega\tau$ has its maximum value at $\gamma = 90^\circ$. Thus, we get for the lifetime $\tau \leq 60$ fs. Within this time both accelerated OH fragments would be separated by $\frac{1}{2} v_f \tau = 110 \text{ pm}$.

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- ²⁰The line shape function can then be written as

$$g(v - v_D) \sim 1 + \beta' P_2\left(\frac{v - v_D}{\Delta v_D}\right) + \beta'' P_4\left(\frac{v - v_D}{\Delta v_D}\right) + \dots;$$
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