

## Correlations between Quantum State Populations of Coincident Product Pairs

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A new method has been developed for determining the correlation of a product molecule with the partner product molecule formed in the same chemical event. Doppler-shift measurements are used in conjunction with level-specific detection of scattered photofragments by laser-induced fluorescence. The technique is demonstrated in the photodissociation of  $\text{H}_2\text{O}_2$  where Doppler profiles of OH absorption lines are used to determine the mean rotational state of the OH partner molecule coincidentally formed in the same fragmentation process.

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The determination of vector correlations has opened a new way to understand the dynamics of chemical events. The correlation between the transition dipole moment  $\mu$  of the parent molecule and the recoil velocity  $\mathbf{v}$  of the fragment, as well as the correlation between  $\mu$  and  $\mathbf{J}$ , the angular momentum of the product, gives information about the symmetry and lifetime of the dissociative state,<sup>1-7</sup> while the  $\langle \mathbf{v} \cdot \mathbf{J} \rangle$  and  $\langle \mu \cdot \mathbf{v} \cdot \mathbf{J} \rangle$  correlations are related to the repulsive force during the fragmentation process.<sup>8-10</sup> If more than one upper electronic state is involved in the dissociation process, then the contribution of each single fragmentation channel to the overall mechanism can be determined by knowledge of the vector correlations between  $\mu$ ,  $\mathbf{v}$ , and  $\mathbf{J}$ .<sup>11</sup> Another important correlation can be gained by a measure of the population of the  $\Lambda$  doublets in linear product molecules with nonzero angular momentum projection along the molecular symmetry axis. The orientation of the unpaired-electron  $p\pi$  lobe lies parallel to  $\mathbf{J}$  for one  $\Lambda$  level, while the other level corresponds to a configuration where the charge density of the unpaired electron is in the plane of rotation.<sup>2,12</sup>

This paper presents a method for the determination of the correlation between the rotational angular momenta of both molecular products formed in the same elementary process. This corresponds to a measure of the state-selected microscopic reaction probabilities  $P(q_A, q_B)$  for formation of the coincident product pairs  $A$  and  $B$  in the quantum states  $q_A$  and  $q_B$ . The method will be illustrated with preliminary results for the photodissociation of hydrogen peroxide yielding two chemically identical hydroxyl fragments.

In general, the photolysis light preferentially selects molecules which have a transition dipole moment  $\mu$  parallel to the electric field vector  $\mathbf{E}$  of the dissociating radiation. This anisotropy of photoselected parent molecules can be transferred to the products. When a selected quantum state  $|i\rangle$  of the ejected fragment is probed with a narrow-bandwidth laser, then the Doppler shift  $(\nu - \nu_0)$  depends on the projection of its velocity along the analyzing laser beam.<sup>13</sup> If the product is formed with a single velocity  $v$  and polarization effects in detection are negligible, then the profile  $D(\nu)$  of each spectral line is given by

$$D(\nu) = \frac{P(i)}{2\Delta\nu_D} \left[ 1 + \beta P_2(\cos\theta) P_2\left(\frac{\nu - \nu_0}{\Delta\nu_D}\right) \right] \quad \text{for } |\nu - \nu_0| \leq \Delta\nu_D, \quad (1)$$

$$D(\nu) = 0 \quad \text{for } |\nu - \nu_0| > \Delta\nu_D,$$

where  $P(i)$  represents the production probability of the fragment  $A$  in state  $|i\rangle$ ,  $\theta$  describes the angle between the  $\mathbf{E}$  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 polynomial, and the maximum Doppler shift  $\Delta\nu_D$  is given by  $\Delta\nu_D = \nu_0(v/c)$ . The anisotropy parameter  $\beta$  contains the information on the vector correlations between  $\mu$ ,  $\mathbf{v}$ , and  $\mathbf{J}$ .

The variation in the Doppler profile with  $\nu$  will vanish if no correlations exist ( $\beta=0$ ), resulting in a rectangular line shape. However, the influence of any anisotropic

fragmentation process on the Doppler profile can also be eliminated if the "magic" observation angle  $\theta_m = 54.7^\circ$ ,  $P_2(\cos\theta_m) = 0$ , is chosen. This is a consequence of the cylindrical geometry involved in the analysis of the fragmentation process. Even if the dissociation takes place in a plane with a very specific scattered angular distribution, observation of the ensemble of ejected products will result in a rectangular Doppler profile.<sup>14</sup>

When the fragments are produced with different velocities,  $v_k$ , then the line shape is given by a summation of

profiles described by Eq. (1),

$$D(v, \theta_m) = \sum_k \frac{P(i, k)}{2\Delta v_D(k)} \theta \left[ 1 + \frac{v - v_0}{\Delta v_D(k)} \right] \theta \left[ 1 - \frac{v - v_0}{\Delta v_D(k)} \right], \quad (2)$$

where  $\Delta v_D(k)$  is the maximum Doppler shift corresponding to  $v_k$ , and  $\theta[x]$  is the step function ( $\theta[x \geq 0] = 1$ ;  $\theta[x < 0] = 0$ ). Obviously, the fragmentation process is subject to several constraints. Conservation of energy demands that the energy  $E_{av}$  before dissociation has to be transferred into translational energy,  $E_t$ , and internal energy,  $E_{int}$ , of the products  $A$  and  $B$ :

$$E_{av} = E_{int}(A) + E_{int}(B) + E_t(A, B), \quad (3)$$

$$E_t(A, B) = \frac{1}{2} m_A v_A^2 + \frac{1}{2} m_B v_B^2. \quad (4)$$

A constraint between  $E_{int}$  and  $E_t$  is further given by the conservation of linear momentum,  $p_A = p_B$ :

$$E_{int}(B) = E_{av} - E_{int}(A) - \frac{1}{2} m_A (1 + m_A/m_B) v_A^2. \quad (5)$$

For a fixed value of the available energy,  $E_{av}$ , the velocities,  $v_A$  and  $v_B$ , of the ejected fragments are quantized if the products  $A$  and  $B$  are formed in discrete eigenstates. The velocity  $v_A$  of the product  $A$  can be measured very accurately by Doppler spectroscopy using a dye laser of sufficiently narrow bandwidth at  $\theta_m = 54.7^\circ$ . Since the internal energy  $E_{int}(A)$  of the product  $A$  is also well

known (laser-induced fluorescence spectroscopy demands knowledge of the initial level  $|i\rangle$ ), the entire product pair state distribution  $P(i, k)$  can be determined by our fitting the observed Doppler profile with Eq. (2). The summation over the levels  $|k\rangle$  of the product  $B$  yields the (classical) product state distribution  $P(i)$  for the product  $A$ ,

$$P(i) = \sum_k P(i, k), \quad (6)$$

and correspondingly  $P(k)$  for the product  $B$ ,

$$P(k) = \sum_i P(i, k). \quad (7)$$

Since the exact observation of one product,  $A$ , determines the microscopic reaction probability  $P(i, k)$ , the population numbers of the other product molecule,  $B$ , can be obtained, even if this fragment  $B$  has "dark" states which cannot be observed by conventional spectroscopic methods. The wings of each spectral line probing level  $|i\rangle$  contain the information about the population of the coincident product partner in state  $|k\rangle$ ; see Eq. (2).

The derivative of the observed line shape with respect to  $v$  yields

$$\frac{\partial D(v, \theta_m)}{\partial v} = \sum_{k=1}^{N_{\max}} \frac{P(i, k)}{2\Delta v_D(k)} \{ \delta[v - v_0 + \Delta v_D(k)] - \delta[v_0 - v + \Delta v_D(k)] \}, \quad (8)$$

resulting in  $2N_{\max}$  peaks at the positions  $v_1(k) = v_0 - \Delta v_D(k)$  and  $v_2(k) = v_0 + \Delta v_D(k)$ , where  $k = 1, 2, \dots, N_{\max}$  labels the quantum states in which the partner product  $B$  is formed, and  $i$  refers to the states of the product  $A$ .  $\delta[x]$  represents the  $\delta$  function. According to Eq. (8), the maximum bandwidth  $\Delta v_1$  of the analyzing dye laser that will resolve the states  $|k\rangle$  and  $|k+1\rangle$  is given by

$$\Delta v_1 \leq |\Delta v_D(k) - \Delta v_D(k+1)|, \quad (9)$$

or with use of Eqs. (3)–(5),

$$\Delta v_1 \leq 2v_0 E_0^{-1/2} | [E - E_{int}(k)]^{1/2} - [E - E_{int}(k+1)]^{1/2} |, \quad (10)$$

with the abbreviations  $E_0 = 2m_A(1 + m_A/m_B)c^2$  and  $E = E_{av} - E_{int}(i)$ . For dissociation processes where most of the available energy is released as translational energy, Eq. (10) simplifies to

$$\Delta v_1 \leq v_0 (E_0 E)^{-1/2} | E_{int}(k+1) - E_{int}(k) |. \quad (11)$$

If the spectral line shape of the analyzing laser light is known, then a significantly higher resolution can be obtained by standard deconvolution methods.

In addition to a very-narrow-bandwidth laser system, two further restrictions have to be considered to obtain the reaction probabilities  $P(i, k)$ . The thermal Doppler motion of the *parent* molecules has to be sufficiently reduced in a molecular beam and the spread of the avail-

able energy  $\Delta E_{av}$  must be small:

$$\Delta E_{av} \approx 2 | E_{int}(k+1) - E_{int}(k) |. \quad (12)$$

$E_{av}$  is determined by the photon energy  $h\nu_P$  of the photolyzing laser light, the internal energy of the parent  $E_{int}(AB)$ , and the dissociation energy  $E_D$ , which is necessary to break the bond between the two fragments  $A$  and  $B$ :

$$E_{av} = h\nu_P + E_{int}(AB) - E_D. \quad (13)$$

Since the internal motion of the parent is also cooled down in a molecular beam, only the bandwidth of the photolyzing light  $\Delta\nu_P$  has to be considered to satisfy Eq.

(12). For example, an ArF excimer laser in broad-band operation has a bandwidth of  $\Delta\nu_P \approx 200 \text{ cm}^{-1}$  and the population numbers of quantum states with a difference in energy of  $|E_{\text{int}}(k+1) - E_{\text{int}}(k)| \approx 100 \text{ cm}^{-1}$  can be measured.

The dissociation energy  $E_D$  can be calculated according to Eqs. (3) and (13). For cooled parent molecules,  $E_{\text{int}}(AB) \approx 0$ , one obtains

$$E_D = h\nu_P - \sum_i \sum_k P(i,k) \{E_{\text{int}}(i) + E_{\text{int}}(k) + E_0[\Delta\nu_D(k)/2\nu_0]^2\}, \quad (14)$$

which allows a direct comparison between spectroscopic and thermodynamic data.

In the photodissociation of  $\text{H}_2\text{O}_2$  at 193 nm, two OH product molecules are formed which are vibrationally cold but rotationally excited. Although both products originating from the same parent are chemically identical, there is, however, *a priori* no reason that their internal energies generated in the *same* dissociation process have to be the same. However, the probability matrix  $P(i,k)$  is symmetric,  $P(i,k) = P(k,i)$ , and consequently the product state distribution of both fragments is identical,  $P(i) = P(k)$ .

The rotational state population can be described by a Gaussian distribution peaking at  $N_P \approx 12$  with a width of  $\Delta N_P \approx 5$  (FWHM).<sup>11,13</sup> In initial experiments, we used a dye laser with a bandwidth of  $0.1 \text{ cm}^{-1}$ , which is not sufficient to resolve the complete rotational state distribution of OH product pairs,  $P(N_A, N_B)$ . However, for a specific rotational state  $N_A$  of one product,  $\text{OH}_A$ , the mean rotational state  $\langle N_B \rangle$  of the other coincidentally formed OH fragment can be determined. The results of such an experiment are shown in Fig. 1. The  $x$  axis represents the rotational state  $N_A$  which is the initial state

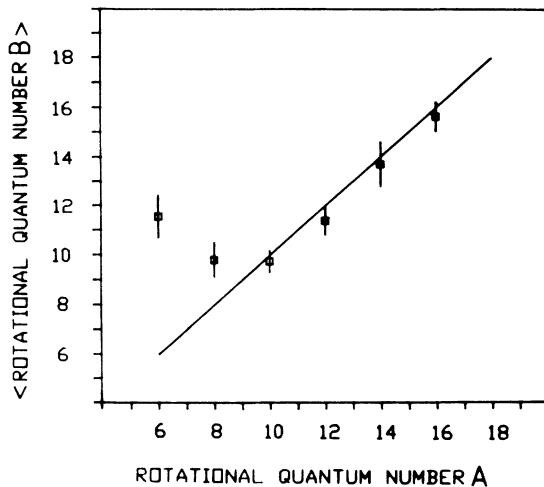


FIG. 1. Correlation between angular momenta of the coincident OH product pairs  $\text{OH}_A$  and  $\text{OH}_B$  formed in the photodissociation of  $\text{H}_2\text{O}_2$  at 193 nm. The abscissa represents a specific rotational state  $N_A$  of the product  $\text{OH}_A$ , while the ordinate represents the mean rotational state  $\langle N_B \rangle$  of the other coincidentally formed OH fragment. The straight line is obtained if the products are formed with the same angular momentum.

to monitor the OH Doppler profile while the ordinate represents the mean rotational state  $\langle N_B \rangle$  obtained via Eqs. (1)–(5). For higher rotational states ( $N > 12$ ) the partner molecules are formed with nearly the same rotation (straight line in Fig. 1),

$$|J_A| \approx |J_B|, \quad (15)$$

indicating a strong correlation between the two rotational vectors of the products of  $\text{OH}_A$  and  $\text{OH}_B$ .

This result is supported by an observation of a strong positive  $\langle \mathbf{v} \cdot \mathbf{J} \rangle$  correlation, showing a preferentially parallel alignment between  $\mathbf{v}$  and  $\mathbf{J}$ .<sup>11</sup> Such an alignment is only possible when the OH radicals are formed via torsional motion of the fragments during fragmentation. For this motion the rotational vectors of the fragments  $\text{OH}_A$  and  $\text{OH}_B$  must point in opposite directions because of conservation of angular momentum,  $\mathbf{J}_A = -\mathbf{J}_B$ . At low rotational states the  $\langle \mathbf{v} \cdot \mathbf{J} \rangle$  correlation decreases because rotation of the OH product originates more from parent symmetric and antisymmetric bending modes or recoil torque. In this case conservation of angular momentum,  $\mathbf{J}_{\text{tot}} = \mathbf{J}_A + \mathbf{J}_B + \mathbf{L}_{AB} \approx 0$ , can always be fulfilled by the orbital angular momentum  $\mathbf{L}_{AB}$ . There-

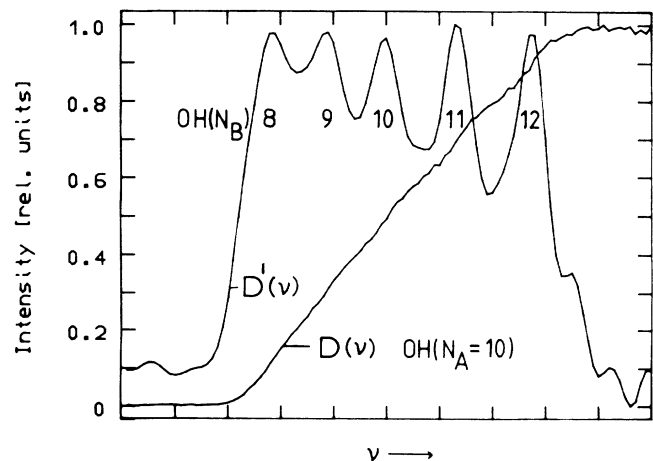


FIG. 2. Wing of a simulated Doppler profile  $D(\nu)$  for the  $Q_1(10)$  line of one  $\text{OH}(N_A=10)$  product in the photofragmentation of  $\text{H}_2\text{O}_2$  at 193 nm. The derivative of  $D(\nu)$  with respect to the frequency of the analyzing dye laser shows the product state distribution of the coincident partner molecule  $\text{OH}(N_B=8-12)$ . A Gaussian noise of 2% and a bandwidth of 100 MHz of the dye laser are assumed.

fore, the restrictive relation, Eq. (15), could be violated. The observation of product pairs (Fig. 1) shows that for rotational states  $N_A < 12$  of the fragment  $\text{OH}_A$ , the mean rotational state ( $N_B$ ) of the partner molecule  $\text{OH}_B$  lies at higher values and consequently the coincident pairs are no longer formed with the same angular momentum. In the lowest populated rotational levels 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  $\text{OH}_B$  is significantly higher than the rotation of the partner molecule  $\text{OH}_A$  as observed in the experiment.

A calculation of the dissociation energy  $E_D$  for the fragmentation of hydrogen peroxide into two OH radicals shows that the obtained value of  $E_D = 196 \text{ kJ mol}^{-1}$  corresponds very well with the value of  $E_D = 207 \text{ kJ mol}^{-1}$  obtained thermodynamically.<sup>15</sup>

We have demonstrated a new method for a direct experimental measurement of microscopic reaction probabilities for two coincident product molecules emerging from the same chemical event. The complete probability matrix  $P(i, k)$  can easily be obtained by the use of a laser system with a sufficiently small bandwidth, e.g., a cw dye laser in combination with a pulsed amplifier. Figure 2 shows one wing of the  $Q_1(10)$  line of a simulated OH Doppler profile in the photodissociation of  $\text{H}_2\text{O}_2$  at 193 nm, where the partner molecule is formed in the rotational states  $N_B = 8-12$  with the same probability. We assumed a bandwidth of  $\Delta\nu_1 = 100 \text{ MHz}$  for the analyzing dye laser and a Gaussian noise of 2%. The derivative of the Doppler profile with respect to the laser frequency reflects the partner distribution, and the modeled probability  $P(N_A = 10, N_B = 8-12)$  can be very well reproduced with a deviation of less than 1% from the true values. A laser system with a bandwidth of 90 MHz is being used in a current experiment to obtain the complete set of correlations between the angular momenta of both OH fragments in the photodissociation of hydrogen peroxide.

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<sup>14</sup>In principle, an extremely directional dissociation process could still cause a variation in the Doppler profile with  $\nu$ . However, in "real" systems these effects are negligible (Refs. 10 and 11) and can be almost completely reduced by the use of unpolarized light for both the photolyzing and the monitoring laser beam.

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