Measurement of the Angular Correlation between Recoil Velocity and Angular Momentum Vectors in Molecular Photodissociation

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A new technique has been developed for determination of the projection of a photofragment's angular momentum vector, **J**, onto its recoil velocity vector, **v**. Doppler-profile spectroscopy is used in conjunction with laser-induced fluorescence probing by polarized light. The technique is illustrated by measurements of the CO Doppler profile following photodissociation of OCS at 222 nm.

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Vector properties are often as important as scalar properties in elucidating the dynamics of molecular interactions. This paper presents a method for determination of the angular correlation between two important vector quantities, the recoil velocity of a photofragment, **v**, and its angular momentum, **J**. The method is based on a combination of velocity analysis by Doppler techniques and angular momentum analysis by polarization techniques. Doppler velocity measurements have been used recently to measure the scattering-angle distribution for bimolecular collisions in molecular beams[1] as well as to determine the angular anisotropy of recoil velocities in photodissociation.[2-4] Polarization techniques have been employed to determine the anisotropic distribution of angular momentum vectors.[2,5,6] However, this is the first report in which the two techniques are combined to measure the angular correlation between velocity and angular momentum vectors. This paper begins by giving a qualitative rationale for the method, proceeds to provide a detailed method for calculation of the Doppler profile from the projection of **J** onto **v**, and ends with an illustration of the method with results for the CO dissociation product of OCS photodissociation.

Consider the photodissociation by linearly polarized light of a molecule into two fragments. It is well known that the probability of finding the recoil velocity vector for the fragments at an angle of θ with respect to the polarization vector of the dissociating light can be described by the function $1+\beta \times P_2(\cos\theta)$.[7,8] A value of β is desired from the Doppler profile of a single internal-energy state of one of the fragments, measured with a tunable probe laser propagating perpendicularly to the direction of the dissociation laser and at an angle θ' with respect to the $\hat{\mathbf{E}}$ vector of the dissociation laser. For fragments of sharply defined kinetic energy $mv_0^2/2$, the probability of finding a recoil velocity vector at an angle χ with respect to the probe beam propagation direction is given by[4]

$$D(\chi,\theta') \propto \int d\phi \, W(\chi,\theta',\phi), \tag{1}$$

where

$$W(\chi,\theta',\phi) = 1+\beta P_2(\cos\theta), \tag{2}$$

with

$$\cos\theta = \cos\theta' \cos\chi + \sin\theta' \sin\chi \sin\phi, \tag{3}$$

and ϕ is the azimuthal angle of **v** about the probe direction as measured from the plane containing the probe direction and the polarization vector of the dissociation laser. The result of the integration is[4]

$$D(\chi,\theta') \propto 2\pi[1+\beta P_2(\cos\chi) P_2(\cos\theta')]. \tag{4}$$

The component of the velocity responsible for the Doppler detuning is $v_0 \cos\chi$. If the fragment has no angular momentum or if **J** is uncorrelated with **v**, Doppler line shapes can be simply analyzed with Eq. (4) to determine β.

We now consider the more general case where **v** and **J** may have an angular correlation. Let one of the fragments be a symmetric-top molecule with angular momentum **J** and let the projection of **J** onto **v** be described by a distribution $P(M_v)$. If there is an angular correlation between **v** and **J**, then the projection of **J** onto **v** will produce a nonstatistical population of M_v levels. For example, if **J** is constrained to be perpendicular to **v**, then $P(M_v=0)=1$ and all other probabilities are zero. Now let the molecule be probed by laser-induced fluorescence (LIF) with light propagating along an axis Z which makes an angle χ with **v**. The projection of $P(M_v)$ onto Z to give $P'(M_J)$ will produce a distribution of M_J values that depends on the angle χ, i.e., one that changes with the velocity probed by the Doppler technique. To pursue the above example, if $\mathbf{J}\perp\mathbf{v}$, then molecules moving with $\mathbf{v}$ parallel to Z will have only $M_J=0$, while those moving with $\mathbf{v}$ perpendicular to Z will have a broad distribution of M_J values. Since polarized light will interact differently with different M_J distributions, the actual LIF Doppler profile will be different from that predicted by Eq. (4). The change in the Doppler profile caused by the $\mathbf{v}$-$\mathbf{J}$ correlation will depend on several factors: the polarization characteristics of the probing light, the angle and polarization acceptance of the detector, and the nature of the absorption and fluorescence transitions. Measurement of the Doppler profile as these factors are varied can be used to uncover the degree of $\mathbf{v}$-$\mathbf{J}$ angular correlation.

Mathematical evaluation of the relationship between the angular correlation and the Doppler profile is straightforward. While elegant tensor methods have been developed recently to describe the interaction of polarized light with molecules,[9,10] for the case under consideration, where only one M_J level might be populated, we have found it more efficient to use an older formalism.[11] The density matrices corresponding to the two basis sets M_v and M_J are related by a unitary transformation[12]:

$$\rho'(\chi,\theta',\phi) = [D(-\phi,\chi,\phi)]^{-1}\rho(\theta)[D(-\phi,\chi,\phi)], \qquad (5)$$

where $\rho(\theta)$ describes the distribution of projections of $\mathbf{J}$ onto $\mathbf{v}$, and $\rho'(\chi,\theta',\phi)$ contains diagonal elements, describing the probabilities for projections of $\mathbf{J}$ onto Z, and off-diagonal elements, describing the coherences. The intensity of laser-induced fluorescence for molecules described by the matrix ρ' is given by[11,13]

$$I(\chi,\theta') \sim \int d\phi\, W(\chi,\theta',\phi)\,\mathrm{Tr}\,\mathbf{AF}, \qquad (6)$$

where W from Eqs. (2)-(3) gives the probability of recoil into a given direction, and the matrices $\mathbf{A}$ and $\mathbf{F}$ describe the absorption and fluorescence steps, respectively. For linear polarization each of these matrices can be described as a sum:

$$\mathbf{A} = \textstyle\sum_F \sum_g \lambda_F \lambda_g \mathbf{A}^{Fg}, \qquad (7)$$

$$\mathbf{F} = \textstyle\sum_F \sum_g \lambda_F \lambda_g \mathbf{F}^{Fg}, \qquad (8)$$

where $F=X,Y,Z$ are the laboratory coordinates, $g=x,y,z$ are the molecular coordinates, and the coefficients λ_F are the projections of the electric vector onto the laboratory coordinates, while the coefficients λ_g are the projections of the dipole moment onto the molecular coordinates. The matrices $\mathbf{A}^{Fg}$ and $\mathbf{F}^{Fg}$ are given by

$$A^{Fg}_{MM'} = \sum \langle J'K'M|\Phi_{Fg}|JKM_J'\rangle \rho'(M_J'M_J) \langle JKM_J|\Phi_{Fg}|J'K'M'\rangle, \qquad (9)$$

$$F^{Fg}_{M'M} = \sum \langle J'K'M'|\Phi_{Fg}|JKM_J\rangle \langle JKM_J|\Phi_{Fg}|J'K'M\rangle, \qquad (10)$$

where the summation is over M_J', M_J from $-J$ to J, $|JKM\rangle$ are the symmetric-top wave functions, and the Φ_{Fg} are the direction cosine matrices, listed elsewhere.[14] For absorption of ± circularly polarized light propagating, for example, along Z, the matrix elements of $\mathbf{A}$ are given by

$$A_{MM'} = \sum \langle J'K'M|\Phi_{Xg} \pm i\Phi_{Yg}|JKM_J'\rangle \rho'(M_J'M_J) \langle JKM_J|\Phi_{Xg} \mp i\Phi_{Yg}|J'K'M'\rangle. \qquad (11)$$

$I(\chi,\theta')$ in Eq. (6) gives the intensity of laser-induced fluorescence as a function of Doppler detuning, χ, for any particular relative angle θ' between the polarization vector of the dissociation laser and the probing direction. If we assume that the weighting function W is known, this equation can be used to examine the relationship between the $\mathbf{v}$-$\mathbf{J}$ correlation and the Doppler profile. In a future publication[15] it will be shown that for $P(M_v)=1$ with $M_v=0$, the off-diagonal elements of ρ', when integrated over ϕ, either are identically zero (for $\beta=0$ or $\theta'=0$) or lead to negligible contributions to the Doppler profile (for example, with circularly polarized probe light). In this case $I(\chi,\theta')$ can be written as a product $D(\chi,\theta',\beta)S(\chi)$, where D is given in Eq. (2) and S is a sensitivity function independent of θ' and β. Further details concerning these calculations will be provided elsewhere,[15] including explicit evaluation of the matrix elements of ρ' and approximations for use when the off-diagonal elements can be ignored.

The method is illustrated by analysis of the Doppler profiles of CO photofragments from the 222-nm dissociation of OCS: $\mathrm{OCS} \rightarrow \mathrm{CO}(v=0,J) + \mathrm{S}(^1D)$.[16,17] As a model of the dissociation, we consider that since the OCS is dissociated from very low rotational levels ($\mathbf{J}_{\mathrm{OCS}} \simeq 0$) and $\mathbf{J}_{\mathrm{OCS}} = \mathbf{L}+\mathbf{J}$, where $\mathbf{L}$ is the orbital angular momentum, it must be true that $\mathbf{L} \simeq -\mathbf{J}$. [We neglect here the angular momentum of $\mathrm{S}(^1D)$, which is much smaller than $\mathbf{J}$.] $\mathbf{L}$ must be perpendicular to $\mathbf{v}$, and so we expect that $\mathbf{J}\perp\mathbf{v}$. In this model, the quantum mechanical description of the state is through the density matrix ρ, which has a single nonzero element, $\rho(M_v,M_v)=1$, when $M_v=0$. The simplified model for the dissociation presented here is consistent with an exact formal treatment for the photofragmentation of triatomic molecules.[18] Under conditions when the initial rotational quantum number of the parent compound is zero, the outgoing scattered wavefunction will be composed of helicity states $\lambda=0,1$. When interference between these states is small, as is the case for the example below, and when the angular momentum quantum number of the diatom is much greater than unity, the exact formalism reduces to the present simplified model. In our experiment the molecular beam is rotationally cooled by supersonic expansion, and the photofragments are produced with high J quantum numbers.

The lower row of panels in Fig. 1 displays the experimental data (dots), and the convolution of the laser linewidth (0.14 cm^{-1} FWHM) with the Doppler profiles predicted by Eq. (6) with $\beta = 0.6$ (solid lines). The upper row of panels shows the convoluted profiles expected in the absence of any **v**-**J** correlation for an anisotropy parameter of $\beta = 0.6$. Along each row, the left-hand panel is for the $Q(59)$ line with the electric vector of the dissociating light $\hat{\mathbf{E}}$ aligned perpendicular to the propagation vector of the probe light Z ($\theta' = 90°$), the second panel is for the $Q(59)$ line with $\hat{\mathbf{E}} \parallel Z(\theta' = 0°)$, the third panel is for the $P(59)$ line with $\hat{\mathbf{E}} \perp Z(\theta' = 90°)$, and the last panel is for the $P(59)$ line with $\hat{\mathbf{E}} \parallel Z(\theta' = 0°)$. The laser linewidth is given as the dashed line in the first panel. It is clear from the figure that line shapes in the presence of **v**-**J** angular correlation (solid lines, bottom row) are qualitatively different from those when there is no correlation (solid lines, top row), and that there are differences in the line shapes depending on the transition probed and the angle θ'. An attempt to fit these data without including the effect of **v**-**J** correlation would lead to different apparent values of β for different θ', as well as incorrect total linewidths. Inclusion of the **v**-**J** correlation is necessary to obtain reasonable fits to the data. Conversely, if one did not know that $\mathbf{J} \perp \mathbf{v}$, as one would not, for example, in the dissociation of a four-atom molecule, the degree of angular correlation between **J** and **v** could be extracted from the data by use of Eqs. (5)–(11) as long as the speed distribution is sharp $[F(v) = \delta(v - v_0)]$. If there is a spread in fragment speeds due to the internal-energy distribution of the unprobed fragment, extraction of the **v**-**J** angular correlation will not be exact, but reasonable approximations may be made.[15]

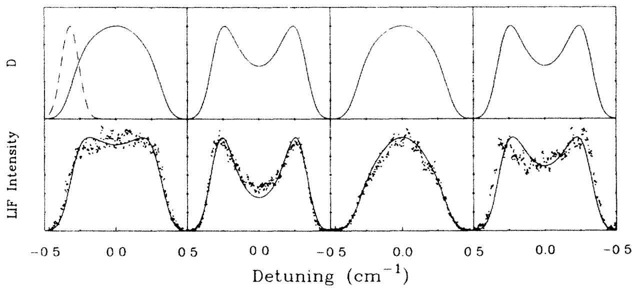

FIG. 1. Experimental and calculated data for the $Q(59)$ and $P(59)$ lines of CO produced in the photodissociation of OCS and probed by laser-induced fluorescence on the CO $A\,{}^1\Pi \leftarrow X\,{}^1\Sigma$ transition using circularly polarized light. The dissociation and LIF probe lasers were orthogonal. Fluorescence was detected without polarization selection at an angle of 45° to each laser beam. Upper row: Doppler profiles expected in the absence of **v**-**J** correlation (solid lines) calculated from Eq. (4); the Gaussian laser linewidth is shown in the dashed curve. Bottom row: Experimental profiles (dots) and profiles calculated for $\mathbf{v} \perp \mathbf{J}$ using Eq. (6) (solid curves). Along each row, the left-hand panel is for the $Q(59)$ line with the electric vector of the dissociating light $\hat{\mathbf{E}}$ aligned perpendicular to the propagation vector of the probe light Z ($\theta' = 90°$), the second panel is for the $Q(59)$ line with $\hat{E} \parallel Z$ ($\theta' = 0°$), the third panel is for the $P(59)$ line with $\hat{E} \perp Z$ ($\theta' = 90°$), and the last panel is for the $P(59)$ line with $\hat{E} \parallel Z$ ($\theta' = 0°$). Calculations using either Eq. (4) or (6) are made with values of $\beta = 0.6$ for the recoil anisotropy, 0.14 cm^{-1} for the FWHM laser linewidth, and 1232 m/s for the velocity, as determined by energy and momentum conservation. The relationship between the angular variable χ and the detuning is $\Delta\nu = (v_0/c)\nu_0 \cos\chi$, where ν_0 is the center frequency and c is the speed of light.

The presence of **v**-**J** angular correlation can be both a benefit and an annoyance. Measurement of the angular correlation provides a new dynamical variable which can help in the understanding of chemical processes. On the other hand, neglect of its effect on the Doppler profile can easily produce misleading results. In photodissociation, the effect might be to assign an incorrect value of β for the dissociation anisotropy, especially if the assignment is based on measurement of the profile at only one orientation of the polarization vector of the dissociating laser. In molecular beam measurements, the effect could lead to an incorrect assignment of the angular scattering distribution, as has already been recognized.[19] For reasons which will be discussed in more detail elsewhere,[15] it appears that, while there are not serious errors in previously published data[1-6] where the Doppler technique has been employed, small corrections to the previous analyses should be made.

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[1] W. D. Phillips, J. A. Serri, D. J. Ely, D. E. Pritchard, K. R. Way, and J. L. Kinsey, Phys. Rev. Lett. **41**, 937 (1978); E. J. Murphy, J. H. Brophy, G. S. Arnold, W. L. Dimpfl, and J. L. Kinsey, J. Chem. Phys. **70**, 5910 (1979); J. A. Serri, A. Morales, W. Moskowitz, D. E. Pritchard,

C. H. Becker, and J. L. Kinsey, J. Chem. Phys. **72**, 6304 (1980); E. J. Murphy, J. H. Brophy, and J. L. Kinsey, J. Chem. Phys. **74**, 331 (1981); J. A. Serri, C. H. Becker, M. B. Elbel, J. L. Kinsey, W. P. Moskowitz, and D. E. Pritchard, J. Chem. Phys. **74**, 5116 (1981); J. A. Serri, J. L. Kinsey, and D. E. Pritchard, J. Chem. Phys. **75**, 663 (1981); W. P. Moskowitz, B. Stewart, R. M. Bilotta, J. L. Kinsey, and D. E. Pritchard, J. Chem. Phys. **80**, 5496 (1984).

[2] R. Vasudev, R. N. Zare, and R. N. Dixon, Chem. Phys. Lett. **96**, 399 (1983), and J. Chem. Phys. **80**, 4863 (1984).

[3] I. Nadler, D. Mahgerefteh, H. Reisler, and C. Wittig, J. Chem. Phys. **82**, 3885 (1985).

[4] R. Schmiedl, H. Dugan, W. Meier, and K. H. Welge, Z. Phys. A **403**, 137 (1982).

[5] P. Andresen and E. W. Rothe, J. Chem. Phys. **78**, 989 (1983); P. Andresen, G. S. Ondrey, B. Titze, and E. Rothe, J. Chem. Phys. **80**, 2548 (1984).

[6] G. E. Hall, N. Sivakumar, and P. L. Houston, "Rotational Alignment of the CN Fragment of ICN Photodissociation," J. Chem. Phys. (to be published).

[7] R. N. Zare and D. R. Herschbach, Proc. IEEE **51**, 173 (1963).

[8] S. Yang and R. Bersohn, J. Chem. Phys. **61**, 4400 (1974).

[9] G. Gouedard and J. C. Lehmann, J. Phys. (Paris) **34**, 693 (1973).

[10] C. H. Greene and R. N. Zare, J. Chem. Phys. **78**, 6741 (1983).

[11] The procedure used here follows R. N. Zare, 1980 Baker Lectures, Cornell University (unpublished); R. N. Zare, private communication; see also R. N. Zare, J. Chem. Phys. **45**, 4510 (1966).

[12] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton Univ. Press, Princeton, N. J., 1957), p. 61.

[13] G. Breit and I. S. Lowen, Phys. Rev. **46**, 590 (1934).

[14] P. C. Cross, R. M. Hainer, and G. W. King, J. Chem. Phys. **12**, 210 (1944).

[15] G. E. Hall, I. Burak, N. Sivakumar, and P. L. Houston, to be published.

[16] N. Sivakumar, I. Burak, W.-Y. Cheung, P. L. Houston, and J. W. Hepburn, J. Phys. Chem. **89**, 3609 (1985).

[17] N. Sivakumar, I. Burak, G. E. Hall, P. L. Houston, and J. W. Hepburn, to be published.

[18] G. G. Balint-Kurti and M. Shapiro, Chem. Phys. **61**, 137 (1981).

[19] D. A. Case, G. M. McClelland, and D. R. Herschbach, Mol. Phys. **35**, 541 (1978).