9660 *J. Phys. Chem. A* **1998,** *102,* 9660−9665

Angular Distributions of Products in the Photodissociation of Diatomic Molecules

James L. Kinsey* and Bruce R. Johnson

Department of Chemistry and Rice Quantum Institute, Rice University, 6100 South Main St., Houston, Texas 77005

Received: June 12, 1998; In Final Form: August 28, 1998

The issue of angular distributions of the products of photodissociation of diatomic molecules is reexamined on two aspects: (1) the nature of the state that is prepared by excitation from a bound level into a continuum, and (2) a demonstration that a semiclassical connection between the *J*-derivative of the scattering phase shift and the classical deflection function leads to a recovery of the classical expression for correction of the angular distribution owing to finite rotation of the molecule during photodissociation. Higher-order quantum contributions to this correction also result from these observations.

I. Introduction

The original and still definitive work on the angular distributions of the fragments produced by photodissociation of diatomic molecules is to be found in the Ph.D. thesis of R. N. Zare[1] and his subsequent publication based on that section of the thesis.[2] Experimental realizations of the seminal ideas contained in Zare's work quickly began to appear.[3−6] Within a very short time, measurement of the angular distributions of photofragments became an essential in the experimentalists' toolbox for studying photodissociative reactions, and it remains so to the present. It is not the intent of this short paper to review the large literature touching on this subject but to comment on two specific issues: (1) the nature of the state that is prepared by excitation into a continuum, and (2) a semiclassical correction for the effects of finite lifetime of the dissociating system and the rotation of the dissociating molecule during the dissociation. The latter point was covered in a classical treatment in Zare's original work, both for diatomics and for polyatomic molecules. Jonah[7] and Yang and Bersohn[8] have also published classical treatments of the finite lifetime/rotation corrections. Siebbeles et al. showed the modifications to the theory for proper treatment of homonuclear diatomics,[9] and Glass-Maujean and Siebbeles[10] have dealt with the angular distributions for excitation along a Fano profile.

II. What Is Prepared in a Bound to Continuum Transition?

This treatment is within the Born−Oppenheimer separation of electronic and vib-rotational variables. We will work in Hund's case a[11,12] and ignore electron spin. We will further assume a transition from a single ground electronic state which supports bound levels to a single excited electronic state with continuum levels. With these assumptions, the total wave function in the ground electronic state can be written as

$$\Psi_{\mathrm{g}}(q,R,\Omega) = \phi^{(\mathrm{g})}(q;R)R^{-1}\psi_{v,J}(R)\left(\frac{2J+1}{8\pi^2}\right)^{1/2} D^{J}_{\Omega,M}(\gamma,\theta,\varphi) \tag{1}$$

Here q is a collective electronic coordinate, R is the internuclear distance; φ and θ are the usual spherical polar angles locating the internuclear axis in space, and γ is a third Eulerian angle specifying the orientation of the "lobe" of the electronic orbital angular momentum wave function relative to the internuclear axis. Alternatively, γ could be arbitrarily set to a fixed value of 0 or $\pi/2$, in which case the normalization factor would be a factor of $\sqrt{2\pi}$ larger than in eq. 1.

The function $\varphi^{(\mathrm{g})}$ is the electronic wave function and $D^{J}_{\Omega,M}$ the Wigner rotation matrix function.[13] Equation 1 adopts the "passive" rather than "active" convention for transformations of coordinate systems.[13,14] The vibrational wave function satisfies a radial Schrödinger equation with the adiabatic Born−Oppenheimer potential $V_{\mathrm{g}}(R)$ plus a centrifugal term $V_{\mathrm{cent}}(R;J,\Omega)$ that depends parametrically on J and Ω:

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2} + V_{\mathrm{g}}(R) + V_{\mathrm{cent}}(R;J,\Omega) - E_{v,J}\right]\psi_{v,J}(R) = 0 \tag{2}$$

where

$$V_{\mathrm{cent}}(R;J,\Omega) = \frac{\hbar^2[J(J+1)-\Omega^2]}{2\mu R^2} \tag{3}$$

$E_{v,J}$ is the energy of the level with vibrational quantum number v and rotational quantum number J. In the ground electronic state, levels with different values of v and J are spaced at discrete intervals from each other.

For the electronically excited state, a similar Born−Oppenheimer expression of the total wave function as the product of electronic, rotational, and radial parts is assumed. However, all energies above the asymptote of the excited electronic state's Born−Oppenheimer potential $V_{\mathrm{ex}}(R)$ are allowed. The wave function for the excited molecule can be written as

$$\Psi_{\mathrm{ex}} = \phi^{(\mathrm{ex})}(q;R)R^{-1}u_{k,J'}(R)\left(\frac{2J'+1}{8\pi^2}\right)^{1/2} D^{J'}_{\Omega',M'}(\gamma,\theta,\varphi) \tag{4}$$

The radial Schrödinger equation for this continuum case becomes

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2} + V_{\mathrm{ex}}(R) + V_{\mathrm{cent}}(R;J',\Omega') - \frac{\hbar^2k^2}{2\mu} - V_{\mathrm{ex}}(R{=}\infty)\right]u_{k,J'}(R) = 0 \tag{5}$$

10.1021/jp9826219 CCC: $15.00

The zero of potential energy in this equation is taken to be the minimum of the ground-state Born−Oppenheimer potential, as it is in eq 2. The quantity $\hbar k$ is the relative momentum of the two atoms at infinite separation in the upper electronic state.

In the asymptotic region, when $V_{\text{ex}}(R) - V_{\text{ex}}(R{=}\infty)$ and $V_{\text{cent}}(R;J',\Omega')$ become negligible, $u_{J',k}(R)$ becomes a linear combination of $\sin(kR)$ and $\cos(kR)$, which we will express as

$$u_{J',k}(R) \sim \sin(kR - J'\pi/2 + \eta_{J'}) \qquad (6)$$

where $\eta_{J'}$ is the scattering phase shift.

This brings us to the question posed in the header of this section: What is prepared in a bound to continuum transition? Most discussions of spectroscopic absorption deal with bound-to-bound transitions, and we are used to thinking that absorption of radiation of the resonant frequency for the transition of one bound state to another bound state results in a preparation of the system in the upper eigenstate. It is very tempting to assume by analogy that in a bound-to-continuum transition one prepares the continuum eigenfunction. That is, the "vibrational" part of the prepared state would be proportional to the solution of eq 5. However, this cannot be the case. The $u_{J',k}(R)$ function in eq 5 has exactly equal incoming and outgoing flux densities of atoms. Otherwise it could not be a stationary state. The actual situation, however, is that we observe *only* outgoing flux and no incoming flux at any value of R.

For the state prepared when the molecule, originally in the ground vibrational state of the lower electronic state, has been exposed to a radiation field of amplitude F_0 for a time T, the correct answer, to first order in the interaction between the radiation field and the molecule, is [15]

$$\chi_{v,J,J'}(R,T) = \frac{iF_0}{2\hbar}\int_0^T \mathrm{d}t\, \exp[i(t - T)\omega]\varphi_{v,J,J'}(R,t) \qquad (7)$$

where $\varphi_{v,J,J'}(R,t)$ is a time-dependent wavepacket moving under the influence of the *excited* electronic state potential $H_{\text{ex},J'}$:

$$\varphi_{v,J,J'}(R,t) = \exp(-iH_{\text{ex},J'}t/\hbar)\hat{\mathbf{e}}\cdot\boldsymbol{\mu}_{\text{g,ex}}(R)\ \psi_{v,J}(R) \qquad (8)$$

Here $\boldsymbol{\mu}_{\text{g,ex}}(R)$ is the *transition moment* for the transition between the two relevant electronic states, $\hat{\mathbf{e}}$ is a unit vector parallel to the polarization of the electromagnetic field, and $\psi_{v,J}(R)$ is the solution to eq 2 for the vth vibrational level of the *initial* electronic state for angular momentum J (usually $v = 0$ for photodissociation experiments). Note the subscript J' in eqs 7 and 8 to remind us that the propagating excited state Hamiltonian includes the centrifugal effective potential for the value of J' that is excited. In the limit that $T \to \infty$, $\chi_{v,J,J'}(R,T)$ is (up to an overall phase) the quantity that Heller and others[15,16−20] have called the "Raman wave function." *If* the upper electronic state has bound eigenstates, and the frequency of the radiation is resonant for excitation of one of these, $\chi_{v,J,J'}(R,T)$ comes to look more and more like the eigenfunction for this bound vibrational state as T gets large. This is beautifully demonstrated in the work of Williams and Imre.[20] Thus, the conventional interpretation is correct for bound-to-bound transitions.

Bound-to-continuum transitions are different. The *imaginary* part of the Raman wave function approaches the continuum eigenfunction (a standing wave) for large T, but there is an equally important *real* part, which is the Hilbert transform of the imaginary part. The imaginary part of $\chi_{v,J,J'}(R,T)$ behaves like $\sin(kR - J'\pi/2 + \eta_{J'})$ for large R, and the real part behaves like $\cos(kR - J'\pi/2 + \eta_{J'})$. Hence, the asymptotic behavior of the prepared state is

$$\chi_{v,J,J'}(R,T) \sim f_{J'}\exp[i(kR - J'\pi/2 + \eta_{J'})] \qquad (9)$$

where $f_{J'}$ is the asymptotic amplitude of $\chi_{0,J,J'}(R,T)$. As required, this function has outgoing flux density and no incoming flux density. It is a traveling wave. It is *not* the solution of the radial Schrödinger equation. This is not a new observation, but it seems to be an issue on which there is so much confusion and error that it is worthwhile stating.

III. General Expression for Angular Distributions of Photoproducts

The foregoing discussion was essentially a vibrational treatment, with the angular behavior left offstage. In actuality, starting from an initial state of angular momentum J, the radiation field coherently prepares amplitudes in electronically excited states with J' equal to $J - 1$, J, and $J + 1$ (P, Q, and R amplitudes, respectively). In general, there will be three slightly different wave packets (because of the differences in the effective centrifugal terms in their driving Hamiltonians) whose half-Fourier transforms will yield slightly different vibrational amplitudes $f_{J'}$. Since all the phase information is incorporated into the phase shifts, the amplitudes $f_{J'}$ are real and nonnegative. The asymptotic behavior of the three wave packets is embodied in the amplitudes $f_{J'}$ and phase shifts $\eta_{J'}$, which provide the ingredients for calculating *any* property of the excited system in the asymptotic region, including "corrections" to the angular distribution expression for finite rotation of the molecule during the process. Beginning with the original work of Zare, there have been many theoretical treatments of the angular distribution of photodissociation products[2,7−10,19,21−24] Our purpose in this section is to show expressions for the angular distributions in terms of the amplitudes and phases, including a connection with the semiclassical deflection function familiar from scattering theory.

For plane polarized light, the space-fixed z-axis can be taken to be the direction of polarization, so that only the space-fixed z-component of the transition matrix is needed. This space-fixed component can be related to body-fixed components by Wigner rotation matrices of order 1.[13]

With incorporation of the angular momentum (including the effect of the vector nature of the transition moment as expressed through its transition from body-fixed to space-fixed components), the expression for the state prepared in the absorption process becomes

$$\Phi_{\text{ex,prepared}} = \phi^{(\text{ex})}(q;R)R^{-1}\sum_{J'}\chi_{0,J,J'}(R)(-1)^{M+\Omega'} \times [(2J'+1)(2J+1)]^{1/2}\begin{pmatrix} J' & 1 & J \\ -\Omega' & p & \Omega \end{pmatrix} \times \begin{pmatrix} J' & 1 & J \\ -M & 0 & M \end{pmatrix}\left(\frac{2J'+1}{8\pi^2}\right)^{1/2} D^{J'}_{\Omega',M}(\gamma,\theta,\varphi) \qquad (10)$$

In this equation the (spherical basis) component p of the transition moment is determined by the values of Ω and Ω' for the participating electronic states: $p = 0$ for parallel transitions and $p = +1$ or -1, depending on whether $\Omega' = \Omega + 1$ or $\Omega' = \Omega - 1$, respectively, for perpendicular transitions (Ω and Ω' are by convention nonnegative numbers). In any event, only a single component p will play a role in the transition between any two specified electronic states.[25] In eq 10, the T dependence of $\chi_{0,J,J'}(R,T)$ has been suppressed. It is understood that T is much longer than the travel time of the wave packet through the region where the potential is significant, in which case the result does not depend significantly on T. The quantities

$$\begin{pmatrix} J' & 1 & J \\ -M & 0 & M \end{pmatrix}$$

etc., are Wigner 3j symbols.

The angular distribution of atoms at a detector very far from the interaction region is obtained for each J and M by calculating the flux density $-i\hbar[\Psi^*(\partial\Psi/\partial R) - \Psi(\partial\Psi^*/\partial R)]$ for Ψ the $\Phi_{\mathrm{ex,prepared}}$ of eq 10. The quantity must then be averaged over a uniform (isotropic) distribution of M's to get the observed angular distribution for the given initial value of J:

$$\sigma_{v,J} = \sum_{J_1,J_2,M} \begin{pmatrix} J_1 & 1 & J \\ -\Omega' & p & \Omega \end{pmatrix}\begin{pmatrix} J_2 & 1 & J \\ -\Omega' & p & \Omega \end{pmatrix} \times \begin{pmatrix} J_1 & 1 & J \\ -M & 0 & M \end{pmatrix}\begin{pmatrix} J_2 & 1 & J \\ -M & 0 & M \end{pmatrix}(2J_1+1)(2J_2+1)f_{J_1}f_{J_2} \times \exp\left[i\left(\frac{J_2\pi}{2} - \frac{J_1\pi}{2} + \eta_{J_1} - \eta_{J_2}\right)\right] D^{J_1}_{\Omega',M}\, D^{*J_2}_{\Omega',M} \quad (11)$$

This can be simplified by the following two identities:[13,14]

$$D^{J_1}_{\Omega',M}\, D^{*J_2}_{\Omega',M} = \sum_K (2K+1)\begin{pmatrix} J_1 & J_2 & K \\ \Omega' & -\Omega' & 0 \end{pmatrix}\begin{pmatrix} J_1 & J_2 & K \\ \mathrm{M} & -M & 0 \end{pmatrix} P_K(\cos\theta) \quad (12)$$

$$\sum_M (-1)^M \begin{pmatrix} J_1 & J_2 & K \\ \mathrm{M} & -M & 0 \end{pmatrix}\begin{pmatrix} J & 1 & J_1 \\ -M & 0 & M \end{pmatrix} \times \begin{pmatrix} J & 1 & J_2 \\ -M & 0 & M \end{pmatrix} = (-1)^J \begin{pmatrix} K & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} K & 1 & 1 \\ J & J_1 & J_2 \end{Bmatrix} \quad (13)$$

The quantity in curly brackets is the Wigner 6j symbol and P_K is the Legendre polynomial of order K. Introducing these into the result of eq 11 yields

$$\sigma_{v,J} = \sum_K (2K+1)(-1)^J \begin{pmatrix} K & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix} P_K(\cos\theta) \times \sum_{J_1,J_2} (2J_1+1)(2J_2+1)f_{J_1}f_{J_2} \exp\left[i\left(\frac{J_2\pi}{2} - \frac{J_1\pi}{2} + \eta_{J_1} - \eta_{J_2}\right)\right] \times (-1)^{\Omega'}\begin{Bmatrix} K & 1 & 1 \\ J & J_1 & J_2 \end{Bmatrix}\begin{pmatrix} J_1 & J_2 & K \\ \Omega' & -\Omega' & 0 \end{pmatrix}\begin{pmatrix} J_1 & 1 & J \\ -\Omega' & p & \Omega \end{pmatrix} \times \begin{pmatrix} J_2 & 1 & J \\ -\Omega' & p & \Omega \end{pmatrix} \quad (14)$$

Because of the appearance of the 3j symbol

$$\begin{pmatrix} K & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix}$$

in this expression, only P_0 (=1) and P_2 terms appear in the angular distribution of the photoproducts, giving the familiar result that

$$\sigma_{v,J}(\theta) = \sigma^0_{v,J} + \sigma^2_{v,J}P_2(\cos\theta) = \sigma^0_{v,J}[1 + \beta P_2(\cos\theta)] \quad (15)$$

with $2 \geq \beta \geq -1$. This simple form is the result of averaging over an isotropic initial distribution in the magnetic quantum number M. Photodissociation from an ensemble with a nonisotropic distribution of M's could lead to a far more complex angular distribution.

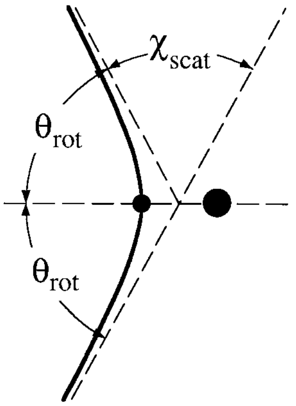

Figure 1. Sketch of trajectory of a projectile atom (small circle) scattering from a stationary target atom (large circle). The dashed line slanting from lower left to upper right is the trajectory in the absence of any interaction between the two atoms. The dashed line slanting from upper left to lower right indicates the asymptote of the actual trajectory. The angle between these two dashed lines is,as indicated, the deflection function χ_{scat}. If, instead of asking how much the trajectory has been deflected from an unimpeded straight line, we ask how much the diatomic system has rotated during this collision, the answer is $\pi - \chi_{\mathrm{scat}}$. This is twice the angle we have defined in the text as $\theta_{\mathrm{rot},J}$. As shown in the figure, the system rotates $\theta_{\mathrm{rot},J}$ in the first half of the collision and another $\theta_{\mathrm{rot},J}$ in the second half. In a photodissociation, the trajectory initiates at the configuration in which the atoms are shown in the figure, and the amount of rotation from the initial orientation of the molecule is *one* $\theta_{\mathrm{rot},J}$.

All the interesting information about photodissociation dynamics is contained in the parameter β. As shown in Zare's original work, the prediction from classical mechanics for negligible rotation of the molecule during the dissociation process (pure axial recoil) is $\beta = 2$ for a parallel transition and $\beta = -1$ for a perpendicular transition.[2] This classical analysis was also extended to provide a correction for the finite rotation of the system during the dissociation in terms of an angle designated as $\theta_{\max}$ by Zare[2] but which we will call $\theta_{\mathrm{rot},J}$ (see Figure 1):

$$\beta_{\mathrm{corrected}} = \beta_0 P_2(\cos\theta_{\mathrm{rot},J}) \quad (16)$$

where β_0 is the appropriate uncorrected value (+2 or −1, respectively, for parallel or perpendicular transitions). Of course, $\beta_{\mathrm{corrected}}$ depends on J through the J-dependence of $\theta_{\mathrm{rot},J}$.

Equation 14 is the most general expression possible for the angular distribution of photoproducts under the very general assumptions stated (Born−Oppenheimer approximation, etc.). All effects such as finite lifetime relative to rotation time must be somehow expressible in the relative values of the different $f_{J'}$ and in the phase shifts.

Because of the

$$\begin{pmatrix} J_1 & J_2 & K \\ \Omega' & -\Omega' & 0 \end{pmatrix}$$

term in eq 14, there are no cross terms between P, Q, and R transitions in $\sigma^0_{v,J}$. In general, $\sigma^2_{v,J}$ has cross terms involving the phase shifts. These cross terms will be proportional to cos($J_2\pi/2 - J_1\pi/2 + \eta_{J_1} - \eta_{J_2}$). It is expedient at this point to make a further approximation:

$$\eta_{J_1} - \eta_{J_2} \approx (J_1 - J_2)(\partial\eta_J/\partial J) \quad (17)$$

so that the argument of the cosine in the cross terms becomes

$(J_1 - J_2)(\partial\eta_J/\partial J - (\pi/2))$. We further introduce the semiclassical relation between the J derivative of the phase shift and the classical deflection function χ_J:[26]

$$\chi_J = 2(\partial\eta_J/\partial J) \tag{18}$$

As shown in Figure 1, χ_J is the angle of *deflection* in the atomic collision at an impact parameter appropriate to the value of J. The angle of *rotation* of the diatomic system in the course of this full collision event is $\pi - \chi_J$, and this is twice the angle of rotation of the diatom in the "half-collision" of a photodissociation, the angle we have called $\theta_{\mathrm{rot},J}$! Hence, a semiclassical connection has been made between scattering theory and the phase of the cos in the cross terms in $\sigma^2_{v,J}$. The P−Q and Q−R cross terms in $\sigma^2_{v,J}$ will be proportional to $\cos(\theta_{\mathrm{rot},J}) = P_1(\theta_{\mathrm{rot},J})$. The P−R cross term will be proportional to $\cos(2\theta_{\mathrm{rot},J})$, which can be expressed as $[4\ P_2(\cos\theta_{\mathrm{rot},J}) - 1]/3$.

The dependence of $f_{J'}$ on J' cannot be expected to have an analog in scattering theory. It is determined by the asymptotic behavior of the half-Fourier transforms of three wave packets moving under slightly different effective potentials. These, in turn, are dependent on the shape of the product of the initial vibrational wave function and the transition moment, not scattering quantities. The expressions can be simplified, however, by approximating the J' dependence of $f_{J'}$ by the first two terms in a power series about $J' = J$. In that case, without loss of generality as far as the shape of the angular distribution is concerned, we can take $f_{\mathrm{P}} = 1 - \Delta$, $f_{\mathrm{Q}} = 1$, $f_{\mathrm{R}} = 1 + \Delta$, where $f_{\mathrm{Q}}\Delta = (\partial f/\partial J)_{\mathrm{Q}}$.

This has brought us about as far as one can go without specializing to either a parallel or a perpendicular transition.

IV. Angular Distributions for a Parallel Transition

For a parallel transition

$$\sigma^0_{v,J} = \frac{f_{\mathrm{P}}{}^2(J^2 - \Omega^2)}{3J(2J+1)} + \frac{f_{\mathrm{Q}}{}^2\Omega^2}{3J(J+1)} + \frac{f_{\mathrm{R}}{}^2[(J+1)^2 - \Omega^2]}{3(J+1)(2J+1)} \tag{19}$$

$$\begin{aligned}\sigma^2_{v,J} = {} & \frac{f_{\mathrm{P}}{}^2(J^2 - \Omega^2)(J^2 - J - 3\Omega^2)}{3J^2(2J+1)^2} + \\ & \frac{f_{\mathrm{Q}}{}^2\Omega^2(J^2 + J - 3\Omega^2)}{3J^2(J+1)^2} + \\ & \frac{f_{\mathrm{R}}{}^2[(J+1)^2 - \Omega^2)][(J+1)(J+2) - 3\Omega^2)]}{3(J+1)^2(2J+1)^2} - \\ & \frac{2f_{\mathrm{P}}f_{\mathrm{R}}[(J^2 - \Omega^2)][(J+1)^2 - \Omega^2)]}{3J(J+1)(2J+1)^2} + \\ & \frac{2\Omega^2 P_1(\cos\theta_{\mathrm{rot},J})}{J(J+1)(2J+1)}\left[\frac{f_{\mathrm{P}}f_{\mathrm{Q}}(J^2 - \Omega^2)}{J} + \frac{f_{\mathrm{Q}}f_{\mathrm{R}}[(J+1)^2 - \Omega^2]}{J+1}\right] + \\ & P_2(\cos\theta_{\mathrm{rot},J})\frac{8f_{\mathrm{P}}f_{\mathrm{R}}(J^2 - \Omega^2)[(J+1)^2 - \Omega^2]}{3J(J+1)(2J+1)^2}\end{aligned} \tag{20}$$

The asymmetry parameter β is the ratio $\sigma^2_{v,J}/\sigma^0_{v,J}$. This is a distressingly complex expression in its full generality. It simplifies greatly, however, if all the amplitudes are assumed to be equal. In that case, we obtain

$$\begin{aligned}\beta_J = {} & 2P_2(\cos\theta_{\mathrm{rot},J})\left[1 - \frac{1}{(2J+1)^2} + \frac{4\Omega^4 - 4\Omega^2(2J^2 + 2J + 1)}{J(J+1)(2J+1)^2}\right] + \\ & \frac{6P_1(\cos\theta_{\mathrm{rot},J})\Omega^2(J^2 + J - \Omega^2)}{J^2(J+1)^2} + \frac{2}{(2J+1)^2} - \\ & \frac{2\Omega^2(4J^2 + 4J - 1)}{J(J+1)(2J+1)^2} + \frac{2\Omega^4(8J^2 + 8J + 3)}{J^2(J+1)^2(2J+1)^2}\end{aligned} \tag{21}$$

The leading term is exactly Zare's expression for the anisotropy parameter for a parallel transition, including his correction for finite rotation of the molecule during the dissociation. Since Ω is usually much smaller than a typical J, the remaining terms are $O(J^{-2})$ or higher.

Alternatively, we can express the anisotropy parameter as a series in the parameter Δ and in $1/(2J + 1)$. This yields the following results:

$$\begin{aligned}\beta_J = {} & 2P_2(\cos\theta_{\mathrm{rot},J}) + \frac{4\Delta(1 - P_2)}{2J+1} - \Delta^2(4P_2 - 1) + \\ & \frac{1}{(2J+1)^2}[-8\Omega^2 + 2 + 24\Omega^2P_1 - (16\Omega^2 + 2)P_2] + \\ & \frac{\Delta^2}{(2J+1)^2}[-4\Omega^2 - 9 - 24\Omega^2P_1 + (40\Omega^2 + \\ & 12)P_2] + O\left(\frac{\Delta}{(2J+1)^3}\right) + O\left(\frac{\Delta^3}{(2J+1)}\right)\end{aligned} \tag{22}$$

V. Angular Distributions for a Perpendicular Transition

When the transition moment is perpendicular to the internuclear axis, the index p of eq 14 has the value 1 or −1, according to whether $\Omega' = \Omega + 1$ or $\Omega' = \Omega - 1$, respectively. We will treat only the $p = 1$ case here. The general expressions for $\sigma^0_{v,J}$ and $\sigma^2_{v,J}$ are

$$\begin{aligned}\sigma^0_{v,J} = {} & \frac{f_{\mathrm{P}}{}^2(J - \Omega)(J - \Omega - 1)}{6J(2J+1)} + \frac{f_{\mathrm{Q}}{}^2(J - \Omega)(J + \Omega + 1)}{6J(J+1)} + \\ & \frac{f_{\mathrm{R}}{}^2(J + \Omega + 1)(J + \Omega + 2)}{6(J+1)(2J+1)}\end{aligned} \tag{23}$$

$$\begin{aligned}\sigma^2_{v,J} = {} & \frac{f_{\mathrm{P}}{}^2(J - \Omega)(J - \Omega - 1)[J^2 - J - 3(\Omega + 1)^2]}{6J^2(2J+1)^2} - \\ & \frac{f_{\mathrm{Q}}{}^2(J - \Omega)(J + \Omega + 1)[J^2 + \mathrm{J} - 3(\Omega + 1)^2]}{6J^2(J+1)^2} + \\ & \frac{f_{\mathrm{R}}{}^2(J + \Omega + 1)(J + \Omega + 2)(J^2 + 3J - 3\Omega^2 - 6\Omega - 1)}{6(J+1)^2(2J+1)^2} + \\ & \frac{f_{\mathrm{P}}f_{\mathrm{R}}(J - \Omega - 1)(J - \Omega)(J + \Omega + 1)(J + \Omega + 2)}{3J(J+1)(2J+1)^2} + \\ & \frac{P_1(\cos\theta_{\mathrm{rot},J})f_{\mathrm{Q}}(J + \Omega + 1)(\Omega + 1)(J - \Omega)}{J(J+1)(2J+1)}\left[\frac{f_{\mathrm{P}}(J - \Omega - 1)}{J} - \frac{f_{\mathrm{R}}(J + \Omega + 2)}{J+1}\right] - \\ & \frac{4P_2(\cos\theta_{\mathrm{rot},J})f_{\mathrm{P}}f_{\mathrm{R}}(J + \Omega + 1)(J + \Omega + 2)(J - \Omega)(J - \Omega - 1)}{3J(J+1)(2J+1)^2}\end{aligned} \tag{24}$$

This completely general expression for the β parameter is even more complicated in form than in the case of the parallel transition. As previously, approximating f_P, f_Q, and f_R as $1 - \Delta$ 1, and $1 + \Delta$ leads to a series expansion in powers of Δ and inverse powers of $(2J + 1)$ with relatively simple leading terms:

$$\beta_J = -P_2(\cos\theta_{\mathrm{rot},J}) + \frac{3}{2}\Delta^2 P_2 + \frac{\Delta}{2J+1}[3 + 2\Omega - 6P_1(\Omega + 1) + P_2(4\Omega + 3)] + \frac{1}{(2J+1)^2}[4\Omega^2 + 8\Omega + 3 - 12(\Omega + 1)^2 P_1 + (8\Omega^2 + 16\Omega + 9)\, P_2] + \frac{\Delta^2}{(2J+1)^2}\left[-10\Omega^2 - 20\Omega - 9 + 6(5\Omega^2 + 9\Omega + 4)P_1 - \left(26\Omega^2 + 46\Omega + \frac{45}{2}\right)P_2\right] + O\left(\frac{\Delta}{(2J+1)^3}\right) + O\left(\frac{\Delta^3}{(2J+1)}\right) \tag{25}$$

When P_1 or P_2 appears without explicit argument, the argument is understood to be $\theta_{\mathrm{rot},J}$.

As in the case of the parallel transition, the leading term of this expansion recaptures the classical result of Zare, including the correction for rotation of the molecule during the dissociation.

VI. Summary and Discussion

In this paper, we have not attempted to treat the β parameter for excitation of a thermal distribution of rotational levels. To accomplish this, one would have to average the expressions in eqs 19 and 20 over a Boltzman distribution, a task complicated by the presence of the $P_1(\cos\theta_{\mathrm{rot},J})$ and $P_2(\cos\theta_{\mathrm{rot},J})$ terms.

For a specific J, we have established a semiclassical connection between the classical correction for rotation of the system during the half-collision. This correction factor, $P_2(\cos\theta_{\mathrm{rot},J})$, will be unity when the rotation angle is near zero. This will typically occur for the smallest values of J, for which the classical deflection function is near π, i.e., when the phase shifts of neighboring partial waves differ by approximately $\pi/2$, *not* when the difference in phase shifts is small. For very large J, the classical deflection function approaches zero, in which case the half-collision rotation angle $\theta_{\mathrm{rot},J}$ approaches $\pi/2$. That is, the β for a parallel transition approaches the value -1 for very large J, and that for a perpendicular transition approaches $+{}^1/_2$, thus making the rotationally corrected parallel result look like the uncorrected perpendicular result! The switching of roles between corrected and uncorrected β's is not as striking in the case of a perpendicular transition, but the corrected result is, even so, closer to that predicted for an uncorrected parallel transition. This is a consequence of fact that the tangential component of velocity for a rotating molecule with sufficiently high angular momentum dominates over the axial recoil velocity. Although this limit is somewhat surprising, it obtains for the classical correction functions for β as well. Fortunately, one seldom deals with extremely large values of J in a spectroscopic study. The range of J's in a spectroscopic experiment is determined by $BJ(J + 1) \sim kT$, where B is the rotational constant for the initial vibrational level of the ground electronic state. In contrast, the range of J in a scattering experiment is determined by $J \sim b\cdot k$, where b is the order of the range of the potential and $\hbar k$ is the momentum.

In the developments in this paper, there has been no transformation from a body-fixed coordinate system determined by the relative *position* of the two nuclei to one determined by their relative *momentum*. This is permissible since all the questions asked about the angular distribution are posed in the asymptotic region, very far from the region of interaction. In that limit these two coordinate systems coincide. For polyatomic molecules this simplification is not possible. However, our recovery of Zare's correction for rotation during dissociation in the diatomic case lends strong support for the use of his correction formulas for polyatomic molecules. Section II is also relevant to polyatomics. The state of a polyatomic molecule that is prepared in a photodissociation is again the half-Fourier transform of a wave packet, initially determined by the ground-state ro-vibrational wave function, and propagated by the Hamiltonian of the electronically excited state. As in the case of the diatomic molecule, this prepared state is *not* one of the stationary continuum states for that Hamiltonian. In the case of the diatomic, we have seen that the angular distribution, at least to the lowest order in our expansion, is determined by the location of the transition moment in the body-fixed axis system and by the scattering phase shifts. It is not likely that a similar result will follow in terms of the S-matrix for scattering of the products in the electronically excited state. The transformed wave packet will produce S-matrix-like quantities that give the fluxes into various channels in the photodissociation. However, the actual S-matrix is designed to give the outgoing fluxes in different channels when the incoming fluxes are determined by incoming scattering conditions, *not* by mapping onto boundary conditions in the interaction region determined by the shape of the ground-state vibrational wave function. Knowing only the S-matrix elements (which describe the incoming and outgoing fluxes in the asymptotic region only) does not provide enough information in itself for satisfying these spectroscopic boundary conditions.

Acknowledgment. This work was supported by the Robert A. Welch Foundation and by National Science Foundation Grant CHE-9528248.

References and Notes

(1) Zare, R. N. Molecular Fluorescence and Photodissociation. Ph.D. Thesis, Harvard University, 1964.

(2) Zare, R. N. *Mol. Photochem.* **1972**, *4*, 1−37.

(3) Wilson, K. R. *Discuss. Faraday. Soc.* **1964**, *44*, 234.

(4) Busch, G. E.; Mahoney, R. T.; Wilson, K. R. *IEEE Quantum Electron* **1970**, *QE-6*, 171.

(5) Busch, G. E.; Mahoney, R. T.; Morse, R. I.; Wilson, K. R. *J. Chem. Phys.* **1969**, *51*, 449.

(6) Solomon, J. *J. Chem. Phys.* **1967**, *47*, 889−895.

(7) Jonah, C. *J. Chem. Phys.* **1971**, *55*, 1915−1922.

(8) Yang, S.-c.; Bersohn, R. *J. Chem. Phys.* **1974**, *61*, 4400−4407.

(9) Siebbeles, L. D. A.; Schins, J. M.; van der Zande, W. J.; Beswich, J. A. *Chem. Phys. Lett.* **1991**, *187*, 633−636.

(10) Glass-Meaujean, M.; Siebbeles, L. D. A. *Phy. Rev. A* **1991**, *44*, 1577−1583.

(11) Lefebvre-Brion, H.; Field, R. W. *Perturbations in the spectra of diatomic molecules*; Academic Press, Inc.: Orlando, FL, 1986.

(12) Herzberg, G. *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules*; D. Van Nostrand Company, Inc.: New York, 1955.

(13) Zare, R. N. *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics*; John Wiley & Sons: New York, 1988.

(14) Edmonds, A. R. *Angular Momentum in Quantum Mechanics*, 2nd ed.; Princeton University Press: Princeton, NJ, 1974.

(15) Johnson, B. R.; Kittrell, C.; Kelly, P. B.; Kinsey, J. L. *J. Phys. Chem.* **1996**, *100*, 7743−7764.

(16) Heller, E. J. *Acc. Chem. Res.* **1981**, *14*, 368−375.

(17) Kulander, K. C.; Heller, E. J. *J. Chem. Phys.* **1978**, *69*, 2439−2449.

(18) Rama Krishna, M. V.; Coalson, R. D. *Chem. Phys.* **1988**, *120*, 327−333.

(19) Jiang, X.-P.; Heather, R.; Metiu, H. *J. Chem. Phys.* **1989**, *90*, 2555−2569.

(20) Williams, S. O.; Imre, D. G. *J. Phys. Chem.* **1988**, *92*, 3363−3374.

(21) Mukamel, S.; Jortner, J. *J. Chem. Phys.* **1974**, *61*, 5348−5357.

(22) Mukamel, S.; Jortner, J. *Chem. Phys. Lett.* **1974**, *29*, 169−173.

(23) Atabek, O.; Beswick, J. A.; Delgado-Barrio, G.; Villareal, P. *Chem. Phys.* **1985**, *95*, 263−271.

(24) Waldeck, J. R.; Shapiro, M.; Bersohn, R. *J. Chem. Phys.* **1993**, *99*, 5924−5835.

(25) Strictly speaking, the rotational wave functions should be symmetrized or antisymmetrized combinations of $D^{J'}_{\Omega',M'}$ and $D^{J'}_{-\Omega',M'}$. This is important in selection rules, but not for the present treatment, since both components are always present and a given p will only connect the "right" ones.

(26) Ford, K. W.; Wheeler, J. A. *Ann. Phys.* **1959**, *7*, 259−286.