Beyond State-to-State Differential Cross Sections: Determination of Product Polarization in Photoinitiated Bimolecular Reactions

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We derive a closed-form expression for the angular momentum polarization (polarization parameters) of the velocity distribution of the $AB(v',J')$ product formed by the reaction sequence $AX + h\nu \rightarrow A + X$ followed by $A + BC(v,J) \rightarrow AB(v',J') + C$. Although in general $(2J' + 1)^2$ parameters are needed to describe the polarization of an arbitrary ensemble of diatomic molecules in a rotational state J', we show that the polarization of the velocity distribution of the $AB(v',J')$ product can be completely specified by $5J'$ dynamically significant polarization parameters. This reduction in the number of degrees of freedom is achieved by introducing a frame of reference we call the stationary-target frame. If the correlation between the relative velocities of the reactants and products and $\mathbf{J}'$ is described with respect to this frame, the polarization-dependent velocity distribution may be written in terms of the $5J'$ polarization-dependent state-to-state differential cross sections $d\sigma_{k0}/d\Omega_r$ (k even), $d\sigma_{k1}/d\Omega_r$, and $d\sigma_{k2}/d\Omega_r$ for which $0 \le k \le 2J'$.
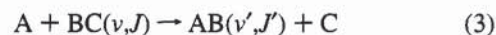
1. Introduction

Crossed molecular beam studies are celebrated[1−3] for providing the probability that the elementary scattering process

$$A + BC \rightarrow AB + C \qquad (1)$$

occurs as a function of the velocities, internal states, and in some cases polarizations of the reactants and products. The dependence of reactivity on these parameters is dictated by the reaction mechanism. For example, a harpoon reaction occurring at a large impact parameter may lead to a rotationally hot, forward-scattered AB product, an abstraction mechanism may lead to a vibrationally hot, back-scattered AB product, and an insertion mechanism that proceeds through a long-lived complex may lead to a statistically populated, equally forward−backward-scattered AB product. Before insight can be gained from a molecular beam experiment, however, laboratory observations must be transformed to a probability of reaction as a function of dynamically significant correlations between the velocity and polarization vectors of the reactants and products. Over the last three decades of molecular beam experiments, methodologies for performing this transformation have become standard. In this paper we extend these methodologies to the study of photoinitiated bimolecular reactions so that these studies can be described using the same language as in crossed-beam scattering experiments.

The study of photoinitiated bimolecular reactions in a single beam (or flow) allows researchers to probe state-to-state differential cross sections and angular momentum polarization with sensitivity and simplicity far greater than those of crossed molecular beam studies.[4−21] In such a photoinitiated reaction study, a gas mixture of AX and BC is expanded into a vacuum chamber. AX is then photodissociated to initiate the reaction sequence:

$$AX + h\nu \rightarrow A + X \qquad (2)$$

$$A + BC(v,J) \rightarrow AB(v',J') + C \qquad (3)$$

A special case of the photoinitiated study of a bimolecular reaction occurs when the BC reagent is in one (or a few) state and the AB product is detected in a state-specific manner. If these requirements are met, then both the center-of-mass speed of the A, BC collision partners and the speed of the $AB(v',J')$ product in the center-of-mass frame are fixed so that a measurement of the distribution of laboratory frame speeds of the $AB(v',J')$ product gives the distribution of reactive scattering angles (i.e., the differential cross section) through application of the law of cosines. We need a name to refer to the growing body of work[4−5,9−21] that exploits this law-of-cosines relationship between product speed and scattering angle. For this purpose, we call these studies "photoloc" (photo law-of-cosines) experiments.

Photoloc measurements give much more product density than do analogous crossed-beam measurements of differential cross sections. This increase in product density has enabled Hall and co-workers,[4,19] Aoiz et al.,[11] Brouard et al.,[9,10,12,17] and Simpson et al.[21] to measure the $AB(v',J')$ product polarization[22] as a function of scattering angle. Such measurements not only determine the probability of reaction as a function of scattering angle but also place constraints on the spatial geometry of the collision as well. As such, these measurements provide new insights into the forces acting between nuclei as reactants are transformed into products.[15,23]

Any realistic photoloc experiment requires careful consideration of the effect of the translational temperature of the (AX, BC) gas mixture, as well as the sensitivity of the experiment to the velocity and polarization of the $AB(v',J')$ product. Unfortunately, these considerations often require sophisticated and experiment-specific analyses that obscure the relationship of the data to the dynamics of the reaction. In this work, we consider an idealized photoloc experiment in which the following conditions are met: (1) the translational temperature of the (AX, BC) gas mixture is 0 K or, equivalently, the thermal averaging caused by the motion of AX and BC is insignificant; (2) the angular momenta of the A and BC(v,J) reactants are completely unpolarized; (3) the photodissociation of AX is achieved by monochromatic, linearly polarized light to produce monoenergetic atoms A with velocities characterized by an anisotropy

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parameter β_{phot}; and (4) the experiment is capable of measuring the polarization of the three-dimensional velocity distribution of the AB(v',J') product. For this idealized photoloc experiment, we measure the three-vector correlation between the polarization of the photolysis laser, the laboratory-frame velocity of the AB product, and the internal angular momentum of the AB product. In the following sections, we obtain a closed-form expression that relates this experimentally measured vector correlation to the dynamically significant three-vector correlation between the relative velocity of the reactants, the relative velocity of the products, and the internal angular momentum of the AB(v',J') product. Although similar conclusions can be drawn from the treatments of Hall and co-workers,[4,19] Brouard et al.,[9,10,12,17] Aoiz et al.,[11] or Orr-Ewing and Zare,[18,20] by limiting ourselves to this idealized experiment, we can make a clear connection to the dynamics of the reaction. Specifically we show that, although the polarization of an arbitrary ensemble of diatomic molecules in a rotational state J' requires $(2J' + 1)^2$ parameters for its full description, the polarization of the AB(v',J') product of a photoinitiated experiment depends on at most $5J'$ dynamically significant polarization parameters. This reduction greatly simplifies the reporting and interpretation of experimental data.

In section 2, we present an overview of the relationship between the differential cross section of a bimolecular reaction and the velocity distribution of the product of a photoinitiated bimolecular reaction. Section 3 introduces frames of reference and notation that allow us to describe the polarization of the differential cross section. Section 4 presents the relationship between the polarization of the velocity distribution of the AB(v',J') product of a photoinitiated reaction and the polarization of the differential cross section. In section 5, we discuss the implications of the planar symmetry of the reaction. In section 6, we present simple recipes for obtaining differential cross sections from quasiclassical trajectory calculations or from quantum mechanical scattering calculations, and we explain how these cross sections may be used to predict the result of realistic photoloc experiments. The appendices contain mathematical details to support the conclusions presented in the text.

2. Relationship between the State-to-State Differential Cross Section and the Velocity Distributions of the AB(v',J') Product

The probability that A and BC(v,J) react to form the products AB(v',J') and C as a function of the laboratory-frame velocities $\mathbf{v}_A$, $\mathbf{v}_{BC}$, $\mathbf{v}_{AB}$, and $\mathbf{v}_C$ can be determined from the state-to-state differential cross section of this reaction. This cross section is a function of only the collision energy E_{col} and the scattering angle θ_r between the relative velocities of the reactants and products. Appendix A reviews the basic kinematics that allow us to make this reduction in degrees of freedom from the twelve velocity components of $\mathbf{v}_A$, $\mathbf{v}_{BC}$, $\mathbf{v}_{AB}$, and $\mathbf{v}_C$ to the two parameters E_{col} and θ_r.

For the idealized photoinitiated reaction described in the previous section, the collision energy is fixed by conservation of energy and momentum:

$$E_{col} = \frac{m_X m_{BC}}{M m_{AX}}(h\nu - D^\circ_{AX}) \tag{4}$$

Here ν is the frequency of the photolysis radiation, D°_{AX} is the dissociation energy of the AX precursor, m_X, m_{BC}, and m_{AX} are the masses of X, BC, and AX, respectively, and $M = m_A + m_{BC} = m_{AB} + m_C$ is the total mass of the reactants or products. Because the collision energy is fixed, the probability of reaction is a function of the scattering angle alone. We denote this

probability by the distribution $P(\cos\theta_r)$. Throughout this paper we use the convention that $P(x_1,x_2,...,x_n)$ denotes a probability distribution in the variables x_1, x_2, ..., x_n normalized so that

$$\int P(x_1,x_2,...,x_n)\,dx_1\,dx_2\,...\,dx_n = 1 \tag{5}$$

Here, the range of integration encompasses the entire n-dimensional space. Thus, the normalization of $P(\cos\theta_r)$ is given by

$$\int_{-1}^{1} P(\cos\theta_r)\,d(\cos\theta_r) = 1 \tag{6}$$

The distribution $P(\cos\theta_r)$ is commonly expressed in terms of the rotational-vibrational-state-to-rotational-vibrational-state differential cross section of the reaction $d\sigma_{vJ \to v'J'}/d\Omega_r$. Because we consider a single rovibrational-state-to-rovibrational-state reaction, we omit the subscript $vJ \to v'J'$ for ease of notation. In the sections that follow, we add a subscript kq to indicate the polarization-dependent cross section, $d\sigma_{kq}/d\Omega_r$. This subscript does not refer to the reactant BC but indicates the polarization of the AB product scattered into the solid angle $d\Omega_r$. The normalization of the differential cross section is defined so that the rate of the state-to-state reaction of eq 3 is given by

$$\frac{dn_{AB}}{dt} = n_A n_{BC} u_r \int_0^{2\pi} \int_{-1}^{1} \frac{d\sigma}{d\Omega_r}\,d(\cos\theta_r)\,d\phi_r$$

$$= n_A n_{BC} u_r \sigma \tag{7}$$

Here, n_A, n_{BC}, and n_{AB} are the number densities of A, BC(v,J), and AB(v',J'), respectively, u_r is the relative speed of the reactants, σ is the integral cross section of the state-to-state reaction, and $d\Omega_r = d(\cos\theta_r)\,d\phi_r$. The normalized probability of reaction is related to the normalized differential cross section by

$$\frac{1}{2\pi}P(\cos\theta_r) = \frac{1}{\sigma}\left(\frac{d\sigma}{d\Omega_r}\right) \tag{8}$$

A photoinitiated experiment determines the differential cross section of a bimolecular reaction because the speed of the center of mass, u, and the speed of the AB(v',J') product in the center-of-mass frame, u_{AB}, are fixed by kinematics. Specifically,

$$u = \left(\frac{2m_A m_X(h\nu - D^\circ_{AX})}{M^2 m_{AX}}\right)^{1/2} \tag{9}$$

and

$$u_{AB} = \frac{m_C}{M}\left(\frac{2(E_{col} - \Delta E)}{\mu'}\right)^{1/2} \tag{10}$$

Here, μ' is the reduced mass of the products, and ΔE is the difference between the energy of formation of the products AB(v',J') and C and the energy of formation of the reactants A and BC(v,J).

In the idealized photoloc experiment, we assume that AX and BC have a 0 K translational temperature. This condition is closely approached by coexpanding AX and BC into a vacuum so that they travel together with the same beam velocity. We define the laboratory frame to be moving with this beam velocity. Consequently, $\mathbf{v}_{BC} = 0$, and the direction of the velocity of the center of mass, $\hat{u}$, is parallel to the direction of the relative velocity of the reactants, $\hat{u}_r$. Additionally, conservation of momentum requires that the direction of the velocity of AB in the center-of-mass frame, $\hat{u}_{AB}$, is parallel to the direction

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of the relative velocity of the products, $\hat{u}_r'$. It follows that

$$\hat{u} \cdot \hat{u}_{AB} = \hat{u}_r \cdot \hat{u}_r' = \cos \theta_r \qquad (11)$$

The speed v_{AB} of the AB product in the laboratory frame can be determined from eqs 9–11 and the relationship

$$\mathbf{v}_{AB} = \mathbf{u} + \mathbf{u}_{AB} \qquad (12)$$

By squaring both sides of eq 12, we find

$$\cos \theta_r = \frac{v_{AB}^2 - u^2 - u_{AB}^2}{2uu_{AB}} \qquad (13)$$

Equation 13 is simply the result of an application of the law of cosines to a triangle with sides of length v_{AB}, u, and u_{AB}. This relationship allows us to use a measurement of the speed of the AB product to determine the scattering angle in a photoloc experiment.

The range of possible product speeds may be determined from eq 13:

$$|u - u_{AB}| \leq v_{AB} \leq |u + u_{AB}| \qquad (14)$$

The speed distribution $P(v_{AB})$ of the $AB(v',J')$ product of the photoinitiated reaction is related to the distribution $P(\cos \theta_r)$ by

$$P(v_{AB})dv_{AB} = P(\cos \theta_r)d(\cos \theta_r) \qquad (15)$$

With the help of eqs 8 and 13, eq 15 becomes

$$P(v_{AB}) = \frac{2\pi v_{AB}}{uu_{AB}} \frac{1}{\sigma}\left(\frac{d\sigma}{d\Omega_r}\right) \qquad (16)$$

In accordance with the convention of eq 5,

$$\int_0^\infty P(v_{AB}) \, dv_{AB} = \int_{|u_{AB}-u|}^{|u_{AB}+u|} P(v_{AB}) \, dv_{AB} = 1 \qquad (17)$$

In eq 16, the differential cross section is evaluated at the value of $\cos \theta_r$ determined by eq 13.

Equation 16 is a remarkable result; it shows that the speed distribution of the $AB(v',J')$ product of the photoinitiated reaction is directly related to the differential cross section for the state-to-state reaction. Thus, a measurement of the speed distribution of the $AB(v',J')$ product determines the normalized differential cross section of this bimolecular reaction. Note that if the mass ratios or energetics are unfavorable, the range of possible speeds of $AB(v',J')$ may be too small to be measured in practice.[13]

The speed distribution of the $AB(v',J')$ product is rarely observed directly. Instead, some component or projection of the three-dimensional velocity distribution $f(\mathbf{v}_{AB})$ is measured. If the photodissociation occurs in such a way that the velocity distribution of A is isotropic ($\beta_{phot} = 0$), then the distribution of $AB(v',J')$ product velocities is isotropic as well. In this case, a trivial relationship exists between $f(\mathbf{v}_{AB})$ and $P(v_{AB})$:

$$f(\mathbf{v}_{AB}) = \frac{1}{4\pi v_{AB}^2}P(v_{AB}) = \frac{1}{2uu_{AB}v_{AB}}\frac{1}{\sigma}\left(\frac{d\sigma}{d\Omega_r}\right) \qquad (\beta_{phot} = 0)$$
$$(18)$$

For an anisotropic photodissociation of AX ($\beta_{phot} \neq 0$), it has been shown[13] that

$$f(\mathbf{v}_{AB}) = \frac{1}{2\pi v_{AB}^2}P(v_{AB}, \cos \theta_\epsilon)$$
$$= \frac{1}{2uu_{AB}v_{AB}}(1 + \beta_{phot}P_2(\cos \theta_u)P_2(\cos \theta_\epsilon))\frac{1}{\sigma}\left(\frac{d\sigma}{d\Omega_r}\right) \qquad (19)$$

Here

$$\cos \theta_u = \hat{u} \cdot \hat{v}_{AB} = \frac{v_{AB}^2 + u^2 - u_{AB}^2}{2u_{AB}u} \qquad (20)$$

and

$$\cos \theta_\epsilon = \hat{\epsilon} \cdot \hat{v}_{AB} \qquad (21)$$

where $\hat{\epsilon}$ gives the direction of the electric vector of the photolyzing radiation determined by the experimental setup and θ_u is equivalent to the variable α of previous papers.[13,14]

Comparison of eq 19 to eq 18 shows that the three-dimensional product velocity distribution in the general case is related to the three-dimensional velocity distribution for the isotropic case by a simple factor. Thus, regardless of the value of the anisotropy parameter β_{phot}, the three-dimensional velocity distribution can always be expressed as the product of a simple term predetermined by kinematics and the dynamically significant normalized differential cross section evaluated at a scattering angle determined by the laboratory-frame speed of the $AB(v',J')$ product. As seen in section 4, a similar separation occurs between the kinematics and dynamics of the experiment when the polarization dependence of the differential cross section is considered. In the discussion that follows, we consider the polarization of the AB product in a classical manner and modify our results so as to be consistent with a quantum mechanical picture of reactive scattering.

3. Scattering, Stationary-Target, and Laboratory Frames of Reference

To quantify the polarization of a diatomic molecule, the direction $\hat{J}'$ of the internal angular momentum of the AB product must be specified with respect to a frame of reference. Here we discuss three relevant frames of reference shown in Figure 1: the scattering frame, the stationary-target frame, and the laboratory frame.

a. Scattering Frame. For unpolarized reactants, the polarization of AB is a result of the direction of the relative velocities of the reactants and products. For this reason, $\hat{J}'$ should be specified with respect to a frame that depends only on $\hat{u}_r = \hat{u}$ and $\hat{u}_r' = \hat{u}_{AB}$. The usual choice of frame of reference is defined by the x^{sc}, y^{sc}, and z^{sc} axes shown in Figure 1a. Here, the z^{sc} axis is parallel to $\hat{u}_r$ and the y^{sc} axis is perpendicular to the plane containing $\hat{u}_r$ and $\hat{u}_r'$. With this choice of coordinates, the $\mathbf{J}'-\mathbf{u}_r-\mathbf{u}_r'$ correlation of the reaction is described by the distribution function $P(\cos \theta_r, \cos \theta_{J'}^{sc}, \phi_{J'}^{sc})$. Here, $\theta_{J'}^{sc}$ and $\phi_{J'}^{sc}$ are the spherical polar angles of $\hat{J}'$, and $P(\cos \theta_r, \cos \theta_{J'}^{sc}, \phi_{J'}^{sc})$ is the probability that the $AB(v',J')$ product is scattered into a differential angle $d(\cos \theta_r)$ about $\cos \theta_r$ with $\hat{J}'$ pointing into a solid angle $d\Omega_{J'}^{sc}) = d(\cos \theta_{J'}^{sc}) d\phi_{J'}^{sc}$. The distribution is normalized according to the convention of eq 5.

b. Stationary-Target Frame. The z^{sc} axis of the scattering frame is chosen to be parallel to $\hat{u}_r$. This choice of coordinate system is well suited to the description of polarization in a crossed beam experiment. It is not well suited, however, to the study of a photoinitiated bimolecular reaction. In a photoloc experiment, we can uniquely determine the laboratory-frame velocity $\mathbf{v}_{AB}$,[15] but we cannot specify $\hat{u}_r = \hat{u} = \hat{z}^{sc}$. For this reason, it is advantageous to describe the $\mathbf{J}'-\mathbf{u}_r-\mathbf{u}_r'$ correlation in a coordinate system in which the z axis is parallel to $\hat{v}_{AB}$
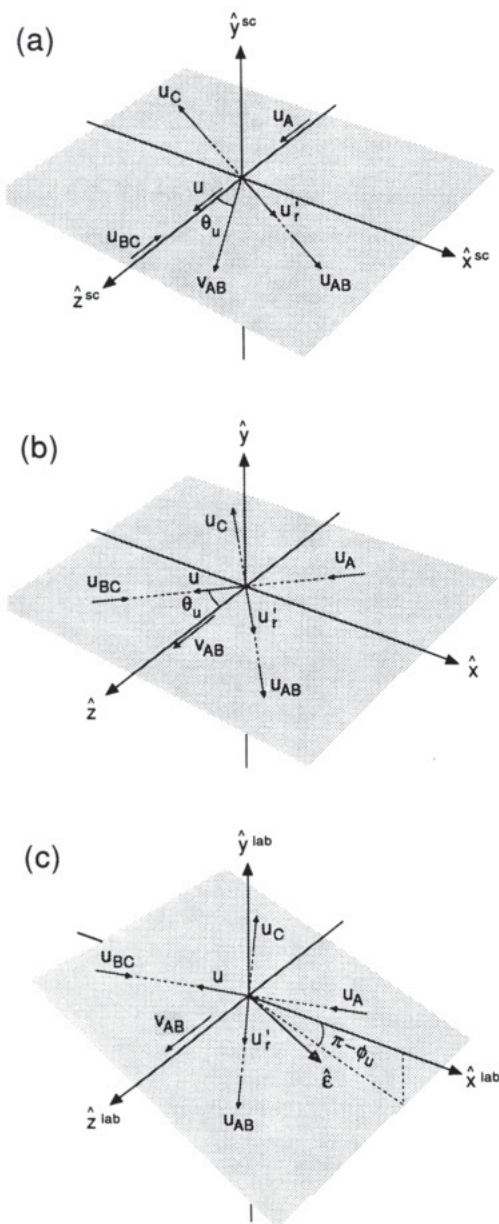
(a)

(b)

(c)

Figure 1. (a) Scattering frame. The z^{sc} axis is parallel to the relative velocities of the reactants $\mathbf{u_r} = \mathbf{u}$ whereas $\hat{\mathbf{y}}^{sc} = \mathbf{u} \times \mathbf{u_r'}/|\mathbf{u} \times \mathbf{u_r'}|$ is perpendicular to the scattering plane. (b) Stationary-target frame. The z axis is parallel to the velocity of the AB product $\mathbf{v_{AB}} = \mathbf{u} + \mathbf{u_{AB}} = \mathbf{u_r} + m_c\mathbf{u_r'}/M$ whereas $\hat{\mathbf{y}} = \hat{\mathbf{y}}^{sc}$ is perpendicular to the scattering plane. (c) Laboratory frame. The z^{lab} axis is parallel to the velocity $\mathbf{v_{AB}} = \mathbf{u} + \mathbf{u_{AB}}$ whereas $\hat{\mathbf{y}}^{lab} = \mathbf{v_{AB}} \times \epsilon/|\mathbf{v_{AB}} \times \epsilon|$ is perpendicular to the plane containing the electric vector of the photolysis radiation, ϵ, and $\mathbf{v_{AB}}$.

rather than to $\hat{\mathbf{u}}$. Such a coordinate system may be created by rotating the scattering frame through an angle θ_u about the y^{sc} axis (Figure 1b). Here, θ_u is the function of v_{AB} given by eq 20. This transformation angle can also be determined from $\cos \theta_r$ and the relation

$$\cos \theta_u = \frac{1 + \gamma \cos \theta_r}{(1 + 2\gamma \cos \theta_r + \gamma^2)^{1/2}} \quad (22)$$

where γ is the parameter defined in a previous work:[13]

$$\gamma = u_{AB}/u$$
$$= \left[\left(\frac{m_{BC}m_C}{m_{AB}m_A} \right) \left(1 - \frac{\Delta E}{E_{col}} \right) \right]^{1/2} \quad (23)$$

We call this rotated reference frame the stationary-target frame.

In this frame, the polarization-dependent probability of reaction is given by $P(\cos \theta_r, \cos \theta_{J'}, \phi_{J'})$, where $\theta_{J'}$ and $\phi_{J'}$ are the spherical polar angles of the direction $\hat{\mathbf{J}}'$.

c. Laboratory Frame. In a photoinitiated reaction, we do not directly measure the $\mathbf{J'}-\mathbf{u_r}-\mathbf{u_r'}$ correlation. Instead, we measure the correlation of $\mathbf{J'}$ with the direction of the laboratory velocity of the AB(v',J') product and the direction of the electric vector of the photolysis radiation. To describe this $\mathbf{J'}-\mathbf{v_{AB}}-\epsilon$ correlation, we define the laboratory frame of reference. This frame is denoted by the axes x^{lab}, y^{lab}, and z^{lab} shown in Figure 1c. The z^{lab} axis is parallel to $\mathbf{v_{AB}}$, and the y^{lab} axis is perpendicular to the plane containing ϵ and $\mathbf{v_{AB}}$. The $\mathbf{J'}-\mathbf{v_{AB}}-\epsilon$ correlation is described by the probability distribution $P(v_{AB}, \cos \theta_\epsilon, \cos \theta_{J'}^{lab}, \phi_{J'}^{lab})$. Here, $\theta_{J'}^{lab}$ and $\phi_{J'}^{lab}$ are the spherical polar angles of $\hat{\mathbf{J}}'$ in the laboratory frame. In section 4, we show that the observable distribution $P(v_{AB}, \cos \theta_\epsilon, \cos \theta_{J'}^{lab}, \phi_{J'}^{lab})$ is directly related to the dynamically significant distribution $P(\cos \theta_r, \cos \theta_{J'}, \phi_{J'})$.

4. Relationship of the Polarization-Dependent Velocity Distribution of the AB(v',J') Product of a Photoinitiated Reaction to the Polarization-Dependent Differential Cross Sectionial Cross Section

The vector correlation $P(\cos \theta_r, \cos \theta_{J'}, \phi_{J'})$ is a fundamental dynamical quantity that may be observed in a photoloc experiment. Unfortunately, we cannot hope to determine this distribution completely. In the idealized photoloc experiment, a measurement of the velocity of the AB(v',J') product fixes the scattering angle θ_r but not the direction normal to the scattering plane. Instead, the observed polarization of the AB product is the reactive polarization averaged over the azimuthal angle about $\mathbf{v_{AB}}$. To visualize the result of this experimental averaging, we consider the reactive scattering of A and BC(v,J) to produce AB(v',J') and C at a fixed scattering angle θ_r. For the purpose of this illustration we assume that the AB(v',J') product rotation is strongly aligned with the y axis, as shown by the contour of $P(\cos \theta_r, \cos \theta_{J'}, \phi_{J'})$ in Figure 2a. The consequence of the averaging is shown in Figure 2b.

To show explicitly how $P(\cos \theta_r, \cos \theta_{J'}, \phi_{J'})$ is related to the result of a photoinitiated experiment, we expand this function in terms of spherical harmonics. The coefficients of this expansion give the polarization parameters of the differential cross section; i.e., the monopole is proportional to the differential cross section and the higher order moments give the dipolar dependence, quadrupolar dependence, etc. of the differential cross section. Explicitly,

$$P(\cos \theta_r, \cos \theta_{J'}, \phi_{J'}) =$$
$$2\pi \sum_{k,q} \left(\frac{1}{\sigma} \frac{d\sigma_{kq}(\cos \theta_r)}{d\Omega_r} \right) \left(\frac{2k+1}{4\pi} \right)^{1/2} Y_{kq}^*(\theta_{J'}, \phi_{J'}) \quad (24)$$

where

$$-k \leq q \leq k \quad (25)$$

and

$$\frac{1}{\sigma} \frac{d\sigma_{kq}(\cos \theta_r)}{d\Omega_r} =$$
$$\frac{1}{2\pi} \left(\frac{4\pi}{2k+1} \right)^{1/2} \int Y_{kq}(\theta_{J'}, \phi_{J'}) P(\cos \theta_r, \cos \theta_{J'}, \phi_{J'}) d\Omega_{J'} \quad (26)$$
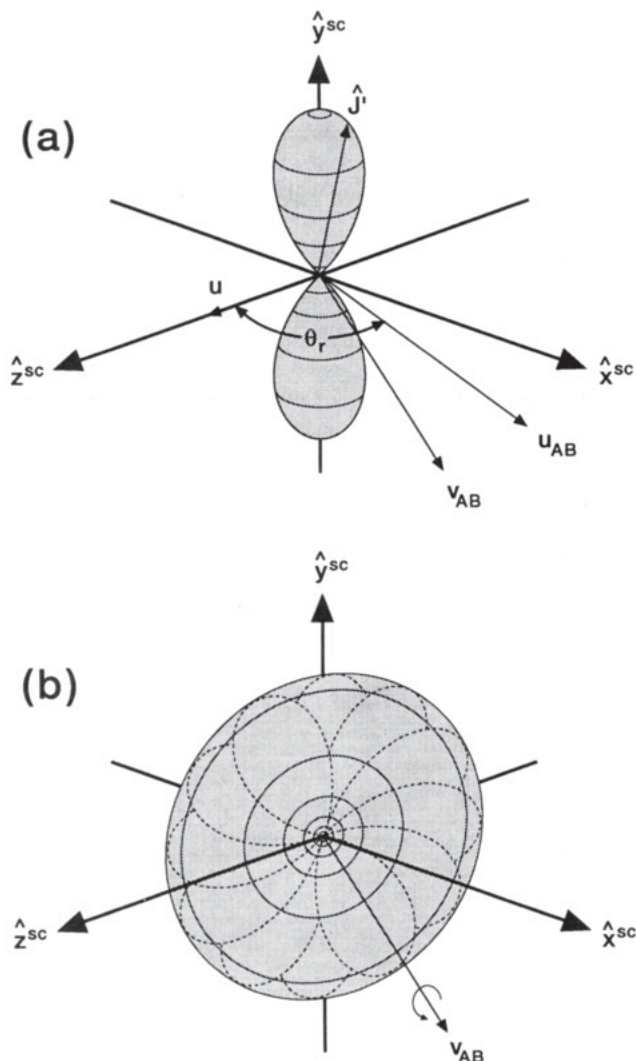
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Figure 2. (a) Distribution of $\hat{\mathbf{J}}'$ associated with a polarized AB(v',J') product scattered into a given angle θ_r. (b) Effect of azimuthal averaging about $\mathbf{v}_{AB}$ on this polarization dependence.

Here, eq 26 is determined by multiplying both sides of eq 24 by $Y_{kq}(\theta_{J'},\phi_{J'})$ and integrating the product over $d\Omega_{J'}$.

Note that the subscript kq indicates that $(1/\sigma)(d\sigma_{kq}/d\Omega_r)$ is a *spherical tensor density*. To obtain the spherical tensor that describes the polarization of the subset of product AB(v',J') molecules scattered into a given volume about the spherical polar angles θ_r and ϕ_r, we must transform $(1/\sigma)(d\sigma_{kq}/d\Omega_r)$ to a frame of reference independent of θ_r and ϕ_r and then integrate over the volume of interest. Each $k-q$ element of $(1/\sigma)(d\sigma_{kq}/d\Omega_r)$ is a polarization-dependent differential cross section. The $k = 0$, $q = 0$ polarization-dependent cross section is equivalent to the differential cross section:

$$\frac{1}{\sigma}\frac{d\sigma_{00}}{d\Omega_r} = \frac{1}{2\pi}\int P(\cos\theta_r,\cos\theta_{J'},\phi_{J'})\,d\Omega_{J'}$$

$$= \frac{1}{2\pi}P(\cos\theta_r)$$

$$= \frac{1}{\sigma}\frac{d\sigma}{d\Omega_r} \qquad (27)$$

From eq 26 and the requirement that $P(\cos\theta_r,\cos\theta_{J'},\phi_{J'})$ is real, we see that the polarization-dependent differential cross sections must have the same symmetry with respect to complex conjugation as the spherical harmonics. Explicitly,

$$\frac{1}{\sigma}\frac{d\sigma_{kq}^*(\cos\theta_r)}{d\Omega_r} = (-1)^q\frac{1}{\sigma}\frac{d\sigma_{k-q}(\cos\theta_r)}{d\Omega_r} \qquad (28)$$

If we integrate eq 24 over all possible values of $\cos\theta_r$, we determine the polarization of the AB product for the case that the orientation of the scattering plane and the direction of $\mathbf{v}_{AB} = \mathbf{u} + \mathbf{u}_{AB}$ are fixed but the scattering angle is unknown. The resulting polarization is described by polarization parameters $a_q^{(k)}$:

$$P(\cos\theta_{J'},\phi_{J'}) = \sum_{k,q}a_q^{(k)}\left(\frac{2k+1}{4\pi}\right)^{1/2}Y_{kq}^*(\theta_{J'},\phi_{J'})$$

$$= \int_{-1}^{1}P(\cos\theta_r,\cos\theta_{J'},\phi_{J'})\,d(\cos\theta_r)$$

$$= \sum_{k,q}\left(2\pi\int_{-1}^{1}\frac{1}{\sigma}\frac{d\sigma_{kq}(\cos\theta_r)}{d\Omega_r}\,d(\cos\theta_r)\right)\times$$

$$\left(\frac{2k+1}{4\pi}\right)^{1/2}Y_{kq}^*(\theta_{J'},\phi_{J'}) \qquad (29)$$

and

$$a_q^{(k)} = 2\pi\int\frac{1}{\sigma}\frac{d\sigma_{kq}(\cos\theta_r)}{d\Omega_r}\,d(\cos\theta_r) \qquad (30)$$

To this point, our discussion has been purely classical. Consistency with quantum mechanics can be made by restricting the range of k so that

$$0 \le k \le 2J' \qquad (31)$$

Hence, for $J' = 1$ the highest polarization moment possible is a quadrapolar alignment with $k = 2$. Equations 25 and 31 imply that $(2J' + 1)^2$ polarization parameters are needed to describe the polarization of a molecule in a state J'. A complete explanation of the polarization parameters and their relationship to the $(2J' + 1)^2$ elements of the density matrix $\varrho_{m'm}$ is given in Appendix B, where we show that

$$a_q^{(k)} =$$

$$\frac{(2J'+1)!}{[(2J'-k)!(2J'+k+1)!]^{1/2}}\sum_{m,m'}(-1)^{J'-m}\begin{pmatrix}J' & J' & k \\ m' & -m & q\end{pmatrix}\varrho_{m'm} \qquad (32)$$

We note that the alignment parameters $a_q^{(k)}$ differ from the usual alignment parameters described by Orr-Ewing and Zare.[18] We have made our choice of alignment parameter so that eq 29 is well defined for all values of J'.

Expanding $P(v_{AB},\cos\theta_\epsilon,\cos\theta_{J'}^{lab},\phi_{J'}^{lab})$ in terms of polarization parameters is useful as well. We define the polarization-dependent velocity distribution $f_{kq}^{lab}(\mathbf{v}_{AB})$ so that

$$P(v_{AB},\cos\theta_\epsilon,\cos\theta_{J'}^{lab},\phi_{J'}^{lab}) =$$

$$2\pi v_{AB}^2\sum_{k,q}f_{kq}^{lab}(\mathbf{v}_{AB})\left(\frac{2k+1}{4\pi}\right)^{1/2}Y_{kq}^*(\theta_{J'}^{lab},\phi_{J'}^{lab}) \qquad (33)$$

where

$$f_{kq}^{lab}(\mathbf{v}_{AB}) = \frac{1}{2\pi v_{AB}^2}\left(\frac{4\pi}{2k+1}\right)^{1/2}\int Y_{kq}(\theta_{J'}^{lab},\phi_{J'}^{lab})\times$$

$$P(v_{AB},\cos\theta_\epsilon,\cos\theta_{J'}^{lab},\phi_{J'}^{lab})\,d\Omega_{J'}^{lab} \qquad (34)$$

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By integrating eq 33 over all directions $\hat{\mathbf{J}}'$ and applying eq 19, we find that the velocity distribution is equivalent to the $k = 0$, $q = 0$ component of the polarization-dependent velocity distribution:

$$f(\mathbf{v}_{AB}) = \frac{1}{2\pi v_{AB}^2} P(v_{AB}, \cos\theta_\epsilon)$$

$$= \frac{1}{2\pi v_{AB}^2} \int P(v_{AB}, \cos\theta_\epsilon, \cos\theta_{J'}^{lab}, \phi_{J'}^{lab}) \, d\Omega_{J'}^{lab}$$

$$= f_{00}^{lab}(\mathbf{v}_{AB}) \tag{35}$$

Integration of eq 33 over all values of v_{AB} and $\cos\theta_\epsilon$ yields the polarization of the $AB(v',J')$ product of a photoloc experiment for which the direction $\hat{v}_{AB}$ and the orientation of the plane containing $\mathbf{v}_{AB}$ and ϵ are fixed but v_{AB} and $\cos\theta_\epsilon$ are unconstrained:

$$P(\cos\theta_{J'}^{lab}, \phi_{J'}^{lab}) = \sum_{k,q} a_q^{(k)\,lab} \left(\frac{2k+1}{4\pi}\right)^{1/2} Y_{kq}^*(\theta_{J'}^{lab}, \phi_{J'}^{lab})$$

$$= \int_{-1}^1 \int_0^\infty P(v_{AB}, \cos\theta_\epsilon, \cos\theta_{J'}^{lab}, \phi_{J'}^{lab}) \, dv_{AB} \times$$
$$d(\cos\theta_e)$$

$$= \sum_{k,q} \left(2\pi \int_{-1}^1 \int_0^\infty v_{AB}^2 f_{kq}^{lab}(\mathbf{v}_{AB}) \, dv_{AB} \, d(\cos\theta_\epsilon)\right) \times$$
$$\left(\frac{2k+1}{4\pi}\right)^{1/2} Y_{kq}^*(\theta_{J'}^{lab}, \phi_{J'}^{lab}) \tag{36}$$

so that

$$a_q^{(k)\,lab} = 2\pi \int_{-1}^1 \int_0^\infty v_{AB}^2 f_{kq}^{lab}(\mathbf{v}_{AB}) \, dv_{AB} \, d(\cos\theta_\epsilon) \tag{37}$$

The parameters $a_q^{(k)\,lab}$ describe the polarization of the $AB(v',J')$ product for an unlikely experiment in which $\hat{v}_{AB}$ is uniquely specified but the photolysis source is an unpolarized laser beam propagating in a direction perpendicular to $\hat{v}_{AB}$. In practice, the laboratory-frame velocity of the AB product is difficult to constrain, whereas the radiation of the photolysis laser is easily polarized. The expected polarization parameters for the more usual case in which the direction $\hat{e}$ is fixed but the velocity $\mathbf{v}_{AB}$ is only partially constrained are given in section 6.

The polarization-dependent velocity distribution $f_{kq}^{lab}(\mathbf{v}_{AB})$ can be determined by convoluting the polarization-dependent differential cross section over all possible scattering planes. In Appendix C, we show that

$$f_{k-q}^{lab}(\mathbf{v}_{AB}) = (-1)^q f_{kq}^{lab}(\mathbf{v}_{AB})^* \tag{38}$$

$$f_{k0}^{lab}(\mathbf{v}_{AB}) = \frac{1}{2uu_{AB}v_{AB}}[1 + \beta_{phot}P_2(\cos\theta_u)P_2(\cos\theta_\epsilon)]\left(\frac{1}{\sigma}\frac{d\sigma_{k0}}{d\Omega_r}\right) \tag{39}$$

$$f_{k1}^{lab}(\mathbf{v}_{AB}) = \frac{-3\beta_{phot}\sin(2\theta_u)}{16uu_{AB}v_{AB}}[\sin(2\theta_\epsilon)]\left(\frac{1}{\sigma}\frac{\sigma_{k1}}{d\Omega_r}\right) \tag{40}$$

$$f_{k2}^{lab}(\mathbf{v}_{AB}) = \frac{3\beta_{phot}\sin^2\theta_u}{16uu_{AB}v_{AB}}[\sin^2\theta_\epsilon]\left(\frac{1}{\sigma}\frac{d\sigma_{k2}}{d\Omega_r}\right) \tag{41}$$

and

$$f_{kq}^{lab}(\mathbf{v}_{AB}) = 0 \qquad \text{for } |q| > 2 \tag{42}$$

Equations 38–42 are key results; they show the separation between the kinematics and the dynamics for the polarization-dependent differential cross section. We conclude that the polarization-dependent velocity distribution depends only on the state-to-state polarization-dependent cross sections $d\sigma_{kq}/d\Omega_r$ for which $|q| \leq 2$. The dependence of the anisotropy of the distribution of $\mathbf{v}_{AB}$ on the value of q was observed by Orr-Ewing and Zare.[18,20] The anisotropy of $\mathbf{v}_{AB}$ for $q = 0$ is described by the speed-dependent anisotropy parameter $\beta(v_{AB}) = \beta_{phot}P_2(\cos\theta_u)$, whereas, for $q = 1$ and $q = 2$, the anisotropy is independent of product speed. The anisotropy of $f_{k1}^{lab}(\mathbf{v}_{AB})$ is of the form $\sin(2\theta_\epsilon)$, and the anisotropy of $f_{k2}^{lab}(\mathbf{v}_{AB})$ is of the form $\sin^2\theta_\epsilon$. This q-dependent anisotropy provides a consistency check for experiments designed to be sensitive to $d\sigma_{k1}/d\Omega_r$ or $d\sigma_{k2}/d\Omega_r$ and indicates that maximum sensitivity to $d\sigma_{k1}/d\Omega_r$ occurs at $\theta_\epsilon = \pi/4$, whereas maximum sensitivity to $d\sigma_{k2}/d\Omega_r$ occurs at $\theta_\epsilon = \pi/2$.

Unfortunately, the first term in eq 40 causes $f_{k1}^{lab}(\mathbf{v}_{AB})$ to vanish when $\sin^2\theta_u = 2\cos\theta_u \sin\theta_u = 0$, and the first term in eq 41 causes $f_{k2}^{lab}(\mathbf{v}_{AB})$ to vanish when $\sin^2\theta_u = 0$. These conditions correspond to a set of scattering angles θ_r that are insensitive to $d\sigma_{k1}/d\Omega_r$ and $d\sigma_{k2}/d\Omega_r$, respectively. Specifically, $f_{k1}^{lab}(\mathbf{v}_{AB})$ vanishes when

$$\cos\theta_u = \frac{1 + \gamma\cos\theta_r}{(1 + 2\gamma\cos\theta_r + \gamma^2)^{1/2}} = 0 \tag{43}$$

and both $f_{k1}^{lab}(\mathbf{v}_{AB})$ and $f_{k2}^{lab}(\mathbf{v}_{AB})$ vanish when

$$\sin^2\theta_u = \frac{\gamma^2(1 - \cos^2\theta_r)}{1 + 2\gamma\cos\theta_r + \gamma^2} = 0 \tag{44}$$

For the forward-scattered and backward-scattered reactions, $\mathbf{v}_{AB}$, $\mathbf{u}_r$, and $\mathbf{u}_r'$ are parallel. This relationship implies that the scattering process has cylindrical symmetry about the $\mathbf{v}_{AB}$ axis. Thus, we expect the polarization-dependent differential cross sections $d\sigma_{kq}/d\Omega_r$ to vanish for the case that $q \neq 0$ and either $\theta_r = 0$ or $\theta_r = \pi$. Thus, the fact that $f_{k1}^{lab}(\mathbf{v}_{AB})$ and $f_{k2}^{lab}(\mathbf{v}_{AB})$ may vanish when $\theta_r = 0$ or $\theta_r = \pi$ is unlikely to hide dynamical information. A more serious problem exists if $\gamma > 1$. In this case the experiment is "blind" to $d\sigma_{k1}/d\Omega_r$ at the scattering angle $\theta_r = \arccos(-1/\gamma)$. It is common to denote these angles as magic angles, but for some purposes perhaps a better name is bewitched.

5. Reflection Symmetry about the Scattering Plane

Although $(2J' + 1)^2$ polarization parameters are required for a complete description of the polarization of an arbitrary ensemble of molecules in a state J', fewer parameters are needed to describe the polarization of the $AB(v',J')$ product of the reactive scattering of an unpolarized atom A and an unpolarized diatomic molecule $BC(v,J)$. This reduction in degrees of freedom is a result of the planar symmetry of the scattering process. Specifically, the probability of finding the nuclear axis of the AB product directed into a solid angle $d(\cos\theta_{n'})d\phi_{n'}$ must be symmetric with respect to the scattering plane

$$P(\cos\theta_r, \cos\theta_{n'}, \phi_{n'}) = P(\cos\theta_r, \cos\theta_{n'}, -\phi_{n'}) \tag{45}$$

This symmetry condition has been shown[24] to require that

$$\frac{1}{\sigma}\frac{d\sigma_{kq}(\cos\theta_r)}{d\Omega_r} \text{ is real for } k \text{ even} \tag{46a}$$

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and

$$\frac{1}{\sigma}\frac{d\sigma_{kq}(\cos\theta_r)}{d\Omega_r} \text{ is imaginary for } k \text{ odd} \quad (46b)$$

Equations 46b and 27 require

$$\frac{1}{\sigma}\frac{d\sigma_{k0}(\cos\theta_r)}{d\Omega_r} = 0 \text{ for } k \text{ odd} \quad (47)$$

Conditions 46 and 47 reduce the number of degrees of freedom necessary to describe the polarization of the $AB(v',J')$ product from $(2J' + 1)^2$ to $2J'(J' + 1)$ if J' is integral and from $(2J' + 1)^2$ to $(2J'(J' + 1) - \frac{1}{2})$ if J' is half-integral.

The symmetry of eq 45 occurs only if the scattering process has a plane of symmetry. Although this symmetry always exists for an atom−diatom reaction, a more general reaction may occur via a chiral pathway that breaks the symmetry of the scattering plane. We also note that the planar symmetry of the scattering process does not imply that the distribution of the angular momentum $\mathbf{J}'$ is symmetric with respect to the scattering plane. Classically, this assymmetry is a result of the fact that $\mathbf{J}' = \mathbf{r}' \times \mathbf{p}'$ is a vector that distinguishes right from left handedness; i.e., the case that $\mathbf{J}'$ is parallel to $\mathbf{u}_r \times \mathbf{u}'_r$ is physically different from the case that $\mathbf{J}'$ is antiparallel to $\mathbf{u}_r \times \mathbf{u}'_r$.

From eqs 39−41, we see that the complex phase of $f_{kq}^{lab}(\mathbf{v}_{AB})$ is identical to that of $d\sigma_{kq}/d\Omega_r$. Thus, the laboratory-frame distribution of the nuclear coordinate of the $AB(v',J')$ product is symmetric with respect to the plane containing $\mathbf{v}_{AB}$ and ϵ if the reaction is symmetric with respect to the scattering plane. Because this symmetry exists in an atom−diatom scattering process, the idealized photoloc experiment defined in the introduction is completely described by the $5J'$ polarization-dependent state-to-state differential cross sections $d\sigma_{k0}/d\Omega_r$ (k even), $d\sigma_{k1}/d\Omega_r$, and $d\sigma_{k2}/d\Omega_r$, for which $0 \leq k \leq 2J'$.

6. Comparison of Theory to Experiment

The stationary-target frame cross sections $d\sigma_{kq}/d\Omega_r$ provide a link that allows theorists and photoloc experimentalists to communicate. In general, only $5J'$ state-to-state polarization-dependent cross sections are needed to describe completely an atom−diatom photoloc experiment in which the A and BC-(v,J) reactants are unpolarized. Furthermore, many photoloc experiments will be sensitive to only those polarization moments with $k = 0$ or $k = 2$. In such cases, all that is needed to compare calculations to experiment is a knowledge of the four cross sections $d\sigma_{00}/d\Omega$, $d\sigma_{20}/d\Omega$, $d\sigma_{21}/d\Omega$, and $d\sigma_{22}/d\Omega$. Even ambitious experimentalists are unlikely to resolve the polarization-dependent cross sections $d\sigma_{kq}/d\Omega_r$ for $k > 4$. For this reason, most photoloc experiments can be described by a manageably small number of polarization-dependent differential cross sections. In this section, we present simple methods for determining $d\sigma_{kq}/d\Omega_r$ from quasiclassical trajectory calculations and quantum mechanical scattering calculations. We conclude by explaining how knowledge of these cross sections may be used to predict the result of typical photoloc experiments.

a. $d\sigma_{kq}/d\Omega_r$ from Quasiclassical Trajectory Calculations. Monte Carlo techniques have been used for over 30 years to determine the differential cross section of chemical reactions. (See for example the 1962 study by Blais and Bunker of the reaction of alkali metals with methyl iodide[25].) To explain how $d\sigma_{kq}/d\Omega_r$ may be calculated from a quasiclassical calculation, we first outline a procedure that might be used to calculate the normalized differential cross section of the $A + BC(v,J) \rightarrow AB$-$(v',J') + C$ scattering process. We then explain how this

procedure could be modified to determine the normalized stationary-target polarization-dependent differential cross sections, $d\sigma_{kq}/d\Omega_r$.

The quasiclassical trajectory calculation of $(1/\sigma)d\sigma/d\Omega$ may proceed as follows: (1) The initial conditions that describe A and $BC(v,J)$ before the reaction are chosen from distributions determined by the laws of quantum mechanics. (2) The motion of the nuclei in the presence of an assumed interaction potential is determined from classical mechanics. If the initial conditions do not lead to the formation of products, step 1 is repeated. If products are formed, the final states v' and J' and the relative velocity $\mathbf{u}'_r$ between the $AB(v',J')$ and C products are determined. The values of the initial relative velocity $\mathbf{u}_r$ and the final velocity $\mathbf{u}'_r$ are used to determine the cosine of the scattering angle, $\cos\theta_r = \hat{\mathbf{u}}_r \cdot \hat{\mathbf{u}}'_r$. (3) The element of an array representing the v−J to v'−J' state-to-state differential cross section associated with $\cos\theta_r$ is increased by a factor of $1/2\pi$. (4) Steps 1−3 are repeated until the differential cross section converges. (5) The differential cross sections are renormalized by the factor $n/2N$, where n is the number of elements in the array representing the differential cross section and N is the total number of trajectories that lead to the creation of AB product in a vibrational state v' and a rotational state J'.

To modify this procedure to determine the normalized stationary-target polarization-dependent differential cross sections, $(1/\sigma)(d\sigma_{kq}/d\Omega_r)$, step 2 must be modified so that the direction $\hat{\mathbf{J}}'$ of the internal angular momentum of the $AB(v',J')$ product is determined as well. In accordance with eq 26, the polarization-dependent differential cross sections $d\sigma_{kq}/d\Omega_r$ may be determined by weighting the trajectory by a factor of

$$\frac{1}{2\pi}\left(\frac{4\pi}{2k+1}\right)^{1/2}Y_{kq}(\theta_{J'},\phi_{J'}) \quad (48)$$

instead of a factor of $1/2\pi$. Here, $\theta_{J'}$ and $\phi_{J'}$ are the stationary-target-frame angles of $\mathbf{J}'$ (see Figure 1). The values of $\theta_{J'}$ and $\phi_{J'}$ may be determined directly from the vectors $\mathbf{u}_r$, $\mathbf{u}'_r$, and $\mathbf{J}'$ and the γ parameter of eq 23:

$$\theta_{J'} = \arccos(\hat{\mathbf{v}}_{AB}\cdot\hat{\mathbf{J}}') \quad (49)$$

and

$$\phi_{J'} = \text{sign}((\hat{\mathbf{u}}_r\times\hat{\mathbf{u}}'_r)\cdot\hat{\mathbf{J}}')\arccot\left(\frac{(\hat{\mathbf{u}}_r\times\hat{\mathbf{u}}'_r)\cdot(\hat{\mathbf{J}}'\times\hat{\mathbf{v}}_{AB})}{(\hat{\mathbf{u}}_r\times\hat{\mathbf{u}}'_r)\cdot\hat{\mathbf{J}}'}\right) \quad (50)$$

Here, $\hat{\mathbf{v}}_{AB} = (\hat{\mathbf{u}}_r + \gamma\hat{\mathbf{u}}'_r)/(1 + 2\gamma\cos\theta_r + \gamma^2)^{1/2}$, and $\text{sign}(x) = 1$ for $x \geq 0$ and $\text{sign}(x) = -1$ for $x < 0$. The symmetry conditions of eqs 46 and 47 may be used as a test of the scattering calculation.

b. $d\sigma_{kq}/d\Omega_r$ from Quantum-Scattering Calculations. We assume that a quantum-scattering calculation is capable of determining the (complex) scattering amplitudes $f_{m_J \rightarrow m_{J'}}^{sc}(\theta_r)$ for the $A + BC(v,J,m_J) \rightarrow AB(v',J',m_{J'}) + C$ reaction. Here m_J is the magnetic quantum number of the reactant, $m_{J'}$ is the magnetic quantum number of the product, and m_J, $m_{J'}$, and $f_{m_J \rightarrow m_{J'}}^{sc}(\theta_r)$ are defined with respect to the scattering frame. For ease of notation we drop the J' subscript from the product magnetic quantum number so that $m_{J'}$ becomes m. The scattering amplitude $f_{m_J \rightarrow m}^{sc}(\theta_r)$ is defined so that, at points far removed from the interaction region, the eigenfunction $\Psi(\mathbf{r}_A, \mathbf{r}_B, \mathbf{r}_C)$ of the reactive Hamiltonian is given by

$$\Psi(\mathbf{r}_A,\mathbf{r}_B,\mathbf{r}_C) = \Psi_{v,J,m_J}(\mathbf{r}_{BC})e^{i\mathbf{k}\cdot\mathbf{r}_{A-BC}} +$$

$$\sum_m \frac{f^{sc}_{m_J\rightarrow m}(\theta_r)}{r_{AB-C}} e^{i\mathbf{k}'\cdot\mathbf{r}_{AB-C}}\Psi_{v',J',m}(\mathbf{r}_{AB}) \quad (51)$$

Here $\Psi_{v,J,m_J}(\mathbf{r}_{BC})$ and $\Psi_{v',J',m}(\mathbf{r}_{AB})$ are the wave functions of the diatomic reactant and product with respect to the scattering frame. The wave number $\mathbf{k}$ is determined by the relative energy of the reactants whereas the wave number $\mathbf{k}'$ is determined by the relative energy of the products. The variable $\mathbf{r}_{A-BC}$ is the relative position vector between the center of masses of the reactants A and BC whereas the variable $\mathbf{r}_{AB-C}$ is the relative position vector between the center of masses of the products AB and C.

If the reactants were to be prepared in a pure quantum state, the density matrix of the product observed to be scattered into differential angle $d\Omega_r = d(\cos\theta_r)\,d\phi_r = d(\cos\theta^{sc})\,d\phi^{sc}$ about θ^{sc} and ϕ^{sc} would be given by

$$\varrho^{sc}_{m'm}(\theta_r) = Nf^{sc*}_{m_J\rightarrow m'}(\theta_r)f^{sc}_{m_J\rightarrow m}(\theta_r) \quad (52)$$

where N is a normalization constant. For the case that the reactants are not prepared in a given magnetic sublevel m_J but instead are described by an isotropic distribution of m_J states, the density matrix becomes

$$\varrho^{sc}_{m'm}(\theta_r) = \frac{N}{2J+1}\sum_{m_J} f^{sc*}_{m_J\rightarrow m'}(\theta_r)f^{sc}_{m_J\rightarrow m}(\theta_r) \quad (53)$$

To determine the normalization constant N, we must integrate $\varrho^{sc}_{m'm}(\theta_r)$ over all scattering angles. Great care must be taken before performing this integration. The density matrix must be expressed with respect to a quantization axis that is independent of the variables of integration, i.e., $\theta_r = \theta^{sc}$ and ϕ^{sc}. This complication can be avoided if we consider the trace of the density matrix. The trace of the density matrix is proportional to the total population of the AB product in a rotational state J' and is therefore independent of the choice of quantization axis. We define N so that the trace of the density matrix becomes equivalent to the normalized differential cross section:

$$\frac{1}{\sigma}\frac{d\sigma}{d\Omega_r} = \sum_m \varrho^{sc}_{mm}(\theta_r) \quad (54)$$

Integrating both sides of eq 54 over $d\Omega_r$, we have

$$1 = \int \left(\sum_m \varrho^{sc}_{mm}(\theta_r)\right) d\Omega_r$$

$$= \frac{N}{2J+1}\int\left(\sum_{m_J,m} f^{sc*}_{m_J\rightarrow m}(\theta_r)f^{sc}_{m_J\rightarrow m}(\theta_r)\right) d\Omega_r \quad (55)$$

so that

$$N = \frac{2J+1}{\int\left(\sum_{m_J,m} f^{sc*}_{m_J\rightarrow m}(\theta_r)f^{sc}_{m_J\rightarrow m}(\theta_r)\right) d\Omega_r} \quad (56)$$

To find the polarization-dependent cross sections with respect to the scattering frame, we apply eq B.15:

$$\frac{1}{\sigma}\frac{d\sigma^{sc}_{kq}}{d\Omega_r} = \frac{(2J'+1)!}{[(2J'-k)!(2J'+k+1)!]^{1/2}} \times$$

$$\sum_{m,m'}(-1)^{J'-m}\begin{pmatrix} J' & J' & k \\ m' & -m & q \end{pmatrix}\varrho^{sc}_{m'm}(\cos\theta_r) \quad (57)$$

Transformation of this polarization-dependent cross section to the stationary-target frame determines the desired polarization-dependent differential cross sections with respect to the stationary-target frame:

$$\frac{1}{\sigma}\frac{d\sigma_{kq}}{d\Omega_r} = \sum_{q'}D^k_{q'q}(\phi_R = 0, \theta_R = \theta_u, \chi_R = 0)\frac{1}{\sigma}\frac{d\sigma^{sc}_{kq'}}{d\Omega_r} \quad (58)$$

Here, θ_u is determined from eq 22.

c. Experimental Predictions from a Knowledge of $d\sigma_{kq}/d\Omega_r$. In section 4 we showed that if we are able to measure the full three-dimensional velocity distribution of the AB product of a single photoinitiated state-to-state reaction, we can determine $d\sigma_{kq}/d\Omega_r$ directly from eqs 39−41. Unfortunately, experimental considerations often prevent such a direct measurement. In many important studies, only the Doppler profile of the AB(v',J') product is measured.[4,6−12,16,17,19] Although these experiments have proved sensitive to the dynamics of bimolecular reactions, the observed polarization-dependent Doppler profiles are not directly related to the polarization-dependent differential cross sections. In this section, we determine an integral relationship between the two.

To find the polarization-dependent Doppler profile, we must average the polarization-dependent velocity distribution over all velocities perpendicular to the direction of the laser propagation. Great care must be taken when averaging the polarization described by $f^{lab}_{kq}(\mathbf{v}_{AB})$ over the experimental range of $\hat{\mathbf{v}}_{AB}$. This average cannot be done directly because the frame of reference that we use to measure the distribution of $\hat{\mathbf{J}}'$ depends on $\hat{\mathbf{v}}_{AB}$. To overcome this problem, we introduce a new frame of reference defined by the axes x^ϵ, y^ϵ, and z^ϵ. Here, the z^ϵ axis is parallel to the electric vector ϵ, whereas the x^ϵ axis is in an arbitrary, yet fixed, direction. The laboratory-frame polarization-dependent velocity distribution $f^{lab}_{kq}(\mathbf{v}_{AB})$ may be transformed to the ϵ-frame polarization-dependent velocity distribution $f^\epsilon_{kq}(\mathbf{v}_{AB})$ by the Wigner rotation matrix $D^k_{q'q}(\phi_R = 0, \theta_R = -\theta^\epsilon_{AB}, \chi_R = -\phi^\epsilon_{AB})$:

$$f^\epsilon_{kq}(\mathbf{v}_{AB}) = \sum_{q'}D^k_{q'q}(\phi_R = 0, \theta_R = -\theta^\epsilon_{AB}, \chi_R = -\phi^\epsilon_{AB})f^{lab}_{kq'}(\mathbf{v}_{AB})$$

$$(59)$$

Here, $\theta^\epsilon_{AB} = \theta_\epsilon$ and $\phi^\epsilon_{AB} = \phi_\epsilon$ are the spherical polar angles of $\hat{\mathbf{v}}_{AB}$ in the ϵ-frame. The z^{lab} axis corresponds to the direction $\hat{\mathbf{v}}_{AB}$, which is the axis of maximum symmetry in a photoloc experiment. By choosing the z^ϵ axis in a direction that does not correspond to $\hat{\mathbf{v}}_{AB}$, we introduce polarization components for which $|q| > 2$. Additionally, we break the one-to-one correspondence between the dynamically significant polarization-dependent differential cross sections and the polarization-dependent velocity distributions. Despite these disadvantages, the ϵ-frame is independent of the AB product velocity $\mathbf{v}_{AB}$. For this reason, $f^\epsilon_{kq}(\mathbf{v}_{AB})$ can be used to calculate the parameters $a^{(k)\epsilon}_q$ that describe the polarization of those AB(v',J') products for which $\mathbf{v}_{min} < \mathbf{v}_{AB} < \mathbf{v}_{max}$:

$$a^{(k)\epsilon}_q = \int_{-v_{min\,x}}^{v_{max\,x}}dv_{ABx}\int_{-v_{min\,y}}^{v_{max\,y}}dv_{ABy}\int_{-v_{min\,z}}^{v_{max\,z}}dv_{ABz}f^\epsilon_{kq}(\mathbf{v}_{AB}) \quad (60)$$

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The variables of integration, v_{ABx}, v_{ABy}, and v_{ABz} may be defined with respect to any coordinate system that is suitable for the problem at hand. If we define this coordinate system so that v_{ABz} corresponds to the velocity along the axis of a probe laser beam, the polarization-dependent Doppler profile, $f_{kq}^{\epsilon}(\omega)$, can be determined:

$$f_{kq}^{\epsilon}(\omega) = \frac{c}{\omega_0} \int_{-\infty}^{\infty} dv_{ABx} \int_{-\infty}^{\infty} dv_{ABy} \, f_{kq}^{\epsilon}(v_{ABx}, v_{ABy}, v_{ABz}) \quad (61)$$

where

$$v_{ABz} = \frac{(\omega - \omega_0)c}{\omega_0} \quad (62)$$

and ω_0 is the frequency of the resonant transition of the $AB(v',J')$ product. Although the averaging over v_{ABx} and v_{ABy} in eq 61 prevents a one-to-one relationship between the probe frequency ω and the scattering angle θ_r, sometimes the polarization-dependent differential cross sections can be reconstructed from a measurement of polarization-dependent Doppler profiles.[9-12,19]

7. Summary and Conclusions

An idealized photoloc experiment, $AX + h\nu \rightarrow A + X$ followed by $A + BC(v,J) \rightarrow AB(v',J') + C$, is defined by the following conditions: (1) The reactant A has a single translational energy determined by the strength of the AX bond and the frequency of the photolysis radiation; (2) AX and BC travel together with the same velocity so that the A + BC collision energy is completely specified; and (3) the internal state of the BC reactant is known and the internal state of the AB product is measured. Under such conditions a measurement of the $AB(v',J')$ velocity gives the correlation between the reactant and product velocities, i.e., the differential cross section, and a measurement of the $AB(v',J')$ polarization gives correlations between the product angular momentum and velocities of the reactants and products, i.e., polarization-dependent differential cross sections. In this paper we present expressions that relate laboratory observations of the AB product velocity and polarization to the differential cross section for the $A + BC(v,J) \rightarrow AB(v',J') + C$ reactive scattering process. These expressions have been cast in the same manner as used to describe crossed molecular beam experiments to allow reactive scattering to be described with a common language.

The results of this paper show that the kinematical and dynamical aspects of experimental data obtained from a photoloc experiment are well separated. Data from experiments that approach the ideal case can be inverted to obtain the dynamically significant polarization-dependent cross sections $d\sigma_{kq}/d\Omega_r$ for $0 \leq q \leq 2$ and k small (typically less than 3). In section 6, we provided simple recipes for determining these polarization-dependent cross sections from scattering calculations and for using these cross sections to predict the results of realistic experiments. The formalism we have presented should help theorists and experimentalists with the interpretation and design of photoloc experiments so that they reveal interesting dynamical effects.

Appendix A. Required Number of Degrees of Freedom To Specify the Velocity Dependence of a Reactive Scattering Process

Consider the probability that the state-to-state reaction $A + BC(v,J) \rightarrow AB(v',J') + C$ occurs as a function of the collision

and escape velocities v_A, v_{BC}, v_{AB}, and v_C. To the uninitiated, the prospect of a complete study of this asymptotic velocity dependence would seem daunting. How is this probability distribution of twelve continuous, independent variables to be communicated, let alone comprehended? Fortunately, the problem is not so difficult as it first appears. By taking advantage of symmetry arguments combined with conservation laws, we show that if the A and $BC(v,J)$ products have no internal polarization and no external forces are at play, the entire velocity dependence of the reaction can be described in terms of two dynamically significant parameters: the *collision energy* and the *scattering angle* of the reaction.[1-3] Here, we review how this reduction in the number of degrees of freedom can be made.

Arbitrary Velocity Frame. The first reduction in the number of degrees of freedom can be made by taking advantage of Galileo's realization that any physical process must not depend on the velocity of the observer. For this reason, we may subtract an arbitrary velocity **u** from each of the velocities of the reactants and products without changing the probability of the reaction. We choose to subtract the velocity of the center of mass,

$$\mathbf{u} = \frac{m_A \mathbf{v}_A + m_{BC} \mathbf{v}_{BC}}{M} \quad (A.1)$$

and write the velocities of the reactants and products in the center-of-mass frame as

$$\mathbf{u}_A = \mathbf{v}_A - \mathbf{u} \quad (A.2)$$

$$\mathbf{u}_{BC} = \mathbf{v}_{BC} - \mathbf{u} \quad (A.3)$$

$$\mathbf{u}_{AB} = \mathbf{v}_{AB} - \mathbf{u} \quad (A.4)$$

and

$$\mathbf{u}_C = \mathbf{v}_C - \mathbf{u} \quad (A.5)$$

This choice of velocity frame has been made so that the linear momentum **P** of the reactants is zero:

$$\mathbf{P} = m_A \mathbf{u}_A + m_B \mathbf{u}_{BC} = 0 \quad (A.6)$$

By taking advantage of eq A.6, we can determine $\mathbf{u}_A$ and $\mathbf{u}_{BC}$ and hence the probability of reaction from the relative velocity $\mathbf{u}_r$. Here

$$\mathbf{u}_r = \mathbf{u}_A - \mathbf{u}_{BC} = \mathbf{v}_A - \mathbf{v}_{BC} \quad (A.7)$$

where

$$\mathbf{u}_A = \frac{m_{BC}}{M} \mathbf{u}_r \quad (A.8)$$

and

$$\mathbf{u}_{BC} = \frac{-m_A}{M} \mathbf{u}_r \quad (A.9)$$

Thus, Galilean symmetry reduces the twelve degrees of freedom to the nine components of $\mathbf{u}_r$, $\mathbf{u}_{AB}$, and $\mathbf{u}_C$.

Conservation of Momentum. Conservation of momentum implies that the momentum of the products must be equal to the momentum of the reactants and hence must be zero in the center-of-mass frame:

$$\mathbf{P} = m_{AB} \mathbf{u}_{AB} + m_C \mathbf{u}_C = 0 \quad (A.10)$$

This relation allows us to determine $\mathbf{u}_{AB}$ and $\mathbf{u}_C$ from the relative velocity of the products, $\mathbf{u}_r'$. Here

$$\mathbf{u}_r' = \mathbf{u}_{AB} - \mathbf{u}_C = \mathbf{v}_{AB} - \mathbf{v}_C \qquad (A.11)$$

where

$$\mathbf{u}_{AB} = \frac{m_C}{M}\mathbf{u}_r' \qquad (A.12)$$

and

$$\mathbf{u}_C = \frac{-m_{AB}}{M}\mathbf{u}_r' \qquad (A.13)$$

Thus, conservation of momentum allows us to reduce the number of dynamically significant parameters to the six components of $\mathbf{u}_r$ and $\mathbf{u}_r'$.

Rotational Symmetry. Provided the reactants are unpolarized with respect to an external reference, the orientation of the frame of reference cannot influence the probability of reaction. This condition allows us to orient our frame of reference to coincide with the relative velocity of the reactants. Thus, only the magnitude and not the direction of the relative velocity of the reactants must be specified. Hence, rotational symmetry reduces the dynamically significant parameters to four: u_r and the three components of $\mathbf{u}_r'$.

Azimuthal Symmetry. If the reactants are unpolarized, the azimuthal scattering angle ϕ_r of the products with respect to the relative velocity of the reactants cannot influence the probability of reaction. Thus, the probability of reaction can be expressed in terms u_r, u_r', and the cosine of the angle θ_r between $\mathbf{u}_r$ and $\mathbf{u}_r'$,

$$\cos\theta_r = \hat{\mathbf{u}}_r \cdot \hat{\mathbf{u}}_r' \qquad (A.14)$$

θ_r is called the scattering angle.

Conservation of Energy. Conservation of energy of the reaction may be written

$$\tfrac{1}{2}m_A v_A^2 + \tfrac{1}{2}m_{BC}v_{BC}^2 + E_{int} = \tfrac{1}{2}m_{AB}v_{AB}^2 + \tfrac{1}{2}m_C v_C^2 + E_{int}' + \Delta D_0 \quad (A.15)$$

where E_{int} and E_{int}' give the internal energies of the reactants and products with respect to their ground states and ΔD_0 gives the difference in energy between the products and reactants both in their ground states. Writing the kinetic energies of the reactants and products in terms of their relative velocities and linear momenta is straightforward:

$$\tfrac{1}{2}m_A v_A^2 + \tfrac{1}{2}m_{BC}v_{BC}^2 = \tfrac{1}{2}\mu u_r^2 + \frac{\mathbf{P}^2}{2M} \qquad (A.16)$$

$$\tfrac{1}{2}m_{AB}v_{AB}^2 + \tfrac{1}{2}m_C v_C^2 = \tfrac{1}{2}\mu' u_r'^2 + \frac{\mathbf{P}^2}{2M} \qquad (A.17)$$

Here, $\mu = m_A m_{BC}/M$ and $\mu' = m_{AB}m_C/M$ are the *reduced masses* of the reactants and products. Equations A.16 and A.17 may be substituted into A.15 to show that

$$u_r' = \left(\frac{\mu u_r^2 - 2\Delta E}{\mu'}\right)^{1/2} \qquad (A.18)$$

where

$$\Delta E = E_{int}' + \Delta D_0 - E_{int} \qquad (A.19)$$

Because we are considering a single state-to-state reaction, ΔE is fixed in value. Thus, once we specify the relative speed of the reactants, u_r, we know the relative velocity of the products. We conclude that the probability of reaction may be specified in terms of the relative speed of the reactants, u_r, and the scattering angle θ_r between the reactants and products. Thus, only two degrees of freedom are required to express the velocity-dependent probability for a state-to-state reaction.

The two terms on the right-hand side of eq A.16 represent the energy available for reaction and the energy associated with the motion of the center of mass. The former is commonly defined to be the collision energy of reaction:

$$E_{col} = \tfrac{1}{2}\mu u_r^2 \qquad (A.20)$$

The probability of a state-to-state reaction is usually stated in terms of E_{col} and $\cos\theta_r$ rather than u_r and θ_r. Thus, the probability of reaction as a function of $\mathbf{v}_A$, $\mathbf{v}_{BC}$, $\mathbf{v}_{AB}$, and $\mathbf{v}_C$ can be predicted by calculating E_{col} and $\cos\theta_r$ from eqs A.7, A.11, A.14, and A.20 and evaluating the probability of reaction, $P(E_{col}, \cos\theta_r)$. Note that the velocities $\mathbf{v}_A$, $\mathbf{v}_{BC}$, $\mathbf{v}_{AB}$, and $\mathbf{v}_C$ do not describe the scattering event completely. To completely describe the trajectories of the reactants and products, the impact parameters must also be considered. For a discussion, see ref 15.

Appendix B. Description of the Polarization of a Molecule

In Appendix A, we showed that, if we are interested only in the velocity dependence of a rovibrational-state to rovibrational-state reaction, the reaction probability may be described in terms of the two parameters E_{col} and θ_r. In this appendix, we determine how many additional parameters are needed to describe the system when we become sensitive to the polarization of the AB(v',J') product.

We know from quantum mechanics that we cannot determine simultaneously the magnitude of the three components of the angular momentum $\mathbf{J}'$ of a system. If we choose a z axis, however, we can determine the component of angular momentum along this axis, J_z'. The value of J_z' is given by the quantum number m' where m' increases in unit steps from $-J'$ to J'. Let us assume we measure J_z' in the scattering frame defined in Figure 1a. In this coordinate system, we may define an m'-dependent differential cross section for the BC(v,J) $\rightarrow$ AB(v',J',m') scattering process:

$$\frac{d\sigma_{vJ \rightarrow v'J'm'}}{d\Omega_r} \qquad (B.1)$$

Although this cross section could be determined from a scattering calculation, it is incomplete because it does not tell us about the projection of J' in the x–y plane. For the case that $m' = 0$, we cannot distinguish the case that $\mathbf{J}'$ lies in the scattering plane from the case that $\mathbf{J}'$ is perpendicular to the scattering plane.

One possible solution is to specify the m'-dependent cross section with respect to several different axes. This approach is, however, a messy solution to the problem. Our choice of coordinate system should be made for the convenience of the calculation at hand. No information should be lost or gained by rotating from one coordinate system to another. The problem is not in our choice of coordinate system but in the fact that the

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m' population does not give a complete description of the $\mathbf{J}'$ dependence of the AB(v',J') product!

To gain a physical picture of what is needed to describe the polarization of the AB product, we imagine a single scattering event. This event may be described by a wave function $\Psi_i(\mathbf{x}_A,\mathbf{x}_B,\mathbf{x}_C,t=0)$ that evolves according to the Schrödinger equation. In general, this wave function will be parametrized by many quantities that describe the initial velocities, positions, and spins of the reactants. As $\Psi_i(\mathbf{x}_A,\mathbf{x}_B,\mathbf{x}_C,t)$ evolves, it distorts so that the AB(v',J') product is discernible. To keep an intuitive picture of the motion of the AB product, we assume that the internal angular momentum is completely described by the orbital motion of the nuclei of A and B as they travel in a spherically symmetric potential. At times far removed from the scattering event, the relative position of the A and B nuclei, $\mathbf{x}_A - \mathbf{x}_B = (r_{n'},\theta_{n'},\phi_{n'})$, is then described by a wave function of the form $\Psi_i(r_{n'})\psi_i(\theta_{n'},\phi_{n'})$. The angular part of this wave function, $\psi_i(\theta_{n'},\phi_{n'})$, can be expanded in terms of angular momentum eigenfunctions $|J',m'\rangle$:

$$\psi_i(\theta_{n'},\phi_{n'}) = \sum_{m'=-J'}^{J'} c_{im'}|J',m'\rangle \tag{B.2}$$

If we know the complex coefficients, $c_{im'}$, we have completely described the AB-polarization dependence of the scattering event defined by the initial conditions i. Moreover, if we know both the real and imaginary parts of the $c_{im'}$ coefficients in one frame, we can use the Wigner rotation matrix to solve for the coefficients in any other frame. Thus, the choice of z axis is arbitrary (as it must be). Because the function $\psi_i(\theta_{n'},\phi_{n'})$ can be expanded in terms of a single set of complex coefficients $c_{im'}$, we consider the wave function to be a *pure state*.

It would appear that our problem is solved. We ran into difficulty in our first attempt to describe the $\mathbf{J}'$ dependence of the differential cross section because we failed to consider the phase of the complex coefficients $c_{im'}$ (i.e., the *coherences* between the m' states). It would seem that although the $2J' + 1$ populations do not suffice to describe the $\mathbf{J}'$ states of the product, the $(2J' + 1) \times 2$ real and imaginary parts of $c_{im'}$ give a complete description of $\mathbf{J}'$. We could imagine defining a complex cross section of the form given by eq B.1 that would give us the probability of reaction as a function of both the phase and magnitude of $c_{im'}$. This approach would make for a fine description of a single scattering event but unfortunately is inadequate to describe a realistic experiment.

A complete description of the $\mathbf{J}'$ dependence of an ensemble of diatomic molecules in a state J' can be defined as a description that allows us to calculate the expectation value of any physical quantity (i.e., Hermitian operator) A. For a single scattering event described by a set of quantum numbers i, the complex coefficients $c_{im'}$ would suffice to calculate the expectation value of A:

$$\langle A\rangle = \langle\psi_i|A|\psi_i\rangle$$
$$= \sum_{m,m'} \langle\psi_i|J',m\rangle\langle J',m|A|J',m'\rangle\langle J',m'|\psi_i\rangle$$
$$= \sum_{m,m'} c_{im}^* A_{mm'} c_{im'} \tag{B.3}$$

We must remember, however, that the polarization of the AB-(v',J') product observed in an experiment corresponds to the average of many scattering events, each with a different set of initial conditions, i. Let us assume that each of these events occurs with a probability $|a_i|^2$ where $0 \le a_i^2 \le 1$. Then the

expectation value of an operator A from all possible scattering events that produce AB(v',J') would be given by

$$\langle A\rangle = \sum_i |a_i|^2 (\sum_{m,m'} c_{im}^* A_{mm'} c_{im'}) \tag{B.4}$$

It might appear that the determination of $\langle A\rangle$ requires a knowledge of the infinite number of coefficients $|a_i|^2$ corresponding to each set of initial conditions, i. Fortunately eq B.4 may be rewritten

$$\langle A\rangle = \sum_{m,m'} (\sum_i |a_i|^2 c_{im}^* c_{im'}) A_{mm'}$$
$$= \sum_{m,m'} \varrho_{m'm} A_{mm'}$$
$$= Tr(\varrho A) \tag{B.5}$$

where $\varrho_{m'm}$ is the density matrix defined by

$$\varrho_{m'm} = \sum_i |a_i|^2 c_{im}^* c_{im'} \tag{B.6}$$

We have just shown that the density matrix provides a complete description of the polarization of an ensemble of diatomic molecules in a state J'; with knowledge of $(2J' + 1)^2$ elements of the density matrix, we can find the expectation value of any Hermitian operator that depends on $\mathbf{J}'$.[24,26]

In the absence of an external field that splits the magnetic sublevels, physical quantities that are related only indirectly to the density matrix are often of interest. The total population, for example, is the trace of the density matrix, whereas the dipole moment of the polarization is a weighted sum of density matrix elements. It is often desirable to consider a description of polarization that is more directly related to these and other fundamental quantities. For this purpose, we introduce the polarization parameters of a system by determining a distribution function $P(\cos\theta_{J'},\phi_{J'})$ that corresponds to the classical probability of finding the vector $\mathbf{J}'$ pointing in the direction described by the spherical polar angles $\theta_{J'}$ and $\phi_{J'}$.

The function $P(\cos\theta_{J'},\phi_{J'})$ may appear incompatible with quantum mechanics because it is a distribution function of two noncommuting operators. For example, if we choose to determine $P(\cos\theta_{J'},\phi_{J'})$ by first fixing $\cos\theta_{J'}$, the value of $\phi_{J'}$ will be completely unconstrained by the uncertainty principle. If, on the other hand, we constrain $\cos\theta_{J'}$ to a narrow range of values, the distribution of $\phi_{J'}$ may exhibit an anisotropy. In fact, we can define $P(\cos\theta_{J'},\phi_{J'})$ in a manner compatible with quantum mechanics provided we describe how the measurement of the distribution is to be made. For this purpose, we assume that $P(\cos\theta_{J'},\phi_{J'})$ is the probability that AB is in the quantum state for which the variance of $\hat{\mathbf{J}}'$ about $\theta_{J'}$ and $\phi_{J'}$ is a minimum. This probability is proportional to the probability $(\varrho_{J'J'})_R$ that the molecule is in a quantum state $m = J'$ when the quantization axis is in a direction given by the spherical polar angles $\theta_{J'}$ and $\phi_{J'}$.

To calculate $P(\cos\theta_{J'},\phi_{J'})$, it is useful to express the density matrix in terms of the moments of the spherical tensor operator $\langle J_q^{(k)}\rangle$ described by Zare[26] and Orr-Ewing and Zare:[18]

$$\langle J_q^{(k)}\rangle = tr(\varrho J_q^{(k)})$$
$$= \sum_{m,m'} \varrho_{m'm}\langle J'm|J_q^{(k)}|J'm'\rangle$$
$$= (J'||J^{(k)}||J') \sum_{m,m'} (-1)^{J'-m}\begin{pmatrix} J' & J' & k \\ m' & -m & q \end{pmatrix}\varrho_{m'm} \tag{B.7}$$

In the last line of eq B.7, we have employed the Wigner–Eckart theorem. Here, $(J'||J^{(k)}||J')$ is the reduced matrix element and the term in brackets is the $3-j$ symbol. The reduced matrix element may be evaluated by taking advantage of methods described in ref 26:

$$(J'||J^{(k)}||J') = k! \left[\frac{(2J'+k+1)!}{2^k(2J'-k)!(2k)!} \right]^{1/2} \quad (B.8)$$

Equation B.8 can be inverted by using the orthogonality properites of the $3-j$ symbols[18,26]

$$\varrho_{m'm} = \sum_{k,q}(-1)^{J'-m}\frac{2k+1}{(J'||J^{(k)}||J')}\begin{pmatrix}J' & J' & k\\ m' & -m & q\end{pmatrix}\langle J_q^{(k)}\rangle \quad (B.9)$$

The probability that a molecule is in magnetic sublevel $m = J'$ is given by the density matrix element $\varrho_{J'J'}$:

$$\varrho_{J'J'} = \sum_k \frac{2k+1}{(J'||J^{(k)}||J')}\begin{pmatrix}J' & J' & k\\ J' & -J' & 0\end{pmatrix}\langle J_0^{(k)}\rangle \quad (B.10)$$

where the $3-j$ symbol may be determined from the expression

$$\begin{pmatrix}J' & J' & k\\ J' & -J' & 0\end{pmatrix} = \frac{(2J')!}{[(2J'-k)!(2J'+k+1)!]^{1/2}} \quad (B.11)$$

The rotational properties of the moments of the spherical tensor operator $\langle J_q^{(k)}\rangle$ allow for a straightforward evaluation of the $m = m' = J'$ component of the density matrix in a coordinate system in which the quantization axis is in a direction given by the spherical polar angles $\theta_{J'}$ and $\phi_{J'}$:

$$(\varrho_{J'J'})_R$$
$$= \sum_{k,q}\frac{2k+1}{(J'||J^{(k)}||J')}\begin{pmatrix}J' & J' & k\\ J' & -J' & 0\end{pmatrix}D_{q0}^k(\phi_R=\phi_{J'}, \theta_R=\theta_{J'},$$

$$\chi_R=0)\langle J_q^{(k)}\rangle$$

$$= \sum_{k,q}\frac{2k+1}{(J'||J^{(k)}||J')}\begin{pmatrix}J' & J' & k\\ J' & -J' & 0\end{pmatrix}\left(\frac{4\pi}{2k+1}\right)^{1/2}Y_{kq}^*(\theta_{J'},\phi_{J'})\langle J_q^{(k)}\rangle$$
$$(B.12)$$

If we wish to relate $(\varrho_{J'J'})_R$ to the probability distribution $P(\cos\theta_{J'},\phi_{J'})$, we first must normalize eq B.12. The orthogonality properties of the spherical harmonic make this integration straightforward:

$$\int(\varrho_{J'J'})_R \, d\Omega_{J'} = \frac{4\pi}{2J'+1} \quad (B.13)$$

so that

$$P(\cos\theta_{J'},\phi_{J'})$$
$$= \frac{2J'+1}{4\pi}(\varrho_{J'J'})_R$$
$$= \sum_{k,q}\frac{(2J'+1)}{(J'||J^{(k)}||J')}\begin{pmatrix}J' & J' & k\\ J' & -J' & 0\end{pmatrix}\langle J_q^{(k)}\rangle\left(\frac{2k+1}{4\pi}\right)^{1/2}Y_{kq}^*(\theta_{J'},\phi_{J'})$$
$$(B.14)$$

By comparing eq B.14 to eq 29 and applying eqs B.8 and B.11, we have

$$a_q^{(k)} = \frac{(2J'+1)}{(J'||J^{(k)}||J')}\begin{pmatrix}J' & J' & k\\ J' & -J' & 0\end{pmatrix}\langle J_q^{(k)}\rangle$$

$$= \frac{(2J'+1)!}{[(2J'-k)!(2J'+k+1)!]^{1/2}}\sum_{m,m'}$$
$$(-1)^{J'-m}\begin{pmatrix}J' & J' & k\\ m' & -m & q\end{pmatrix}\varrho_{m'm} \quad (B.15)$$

To relate the polarization parameters $a_q^{(k)}$ to the more usual polarizationparameters $\mathscr{A}_q^{(k)}$ described by Orr-Ewing and Zare,[18] we write

$$a_q^{(k)} = \frac{c(k,J')}{(J(J+1))^{k/2}}\langle J_q^{(k)}\rangle \quad (B.16)$$

Equations B.8, B.11, and B.15 can be used to show that

$$c(k,J') = \left(\frac{(2k-1)!!}{k!}\right)^{1/2}\left[\frac{(2J'+1)!2^k(J'(J'+1))^{k/2}}{(2J'+1+k)!}\right] \quad (B.17)$$

The limiting value of $c(k,J')$ as J' approaches infinity gives the alignment parameters $\mathscr{A}_q^{(k)}$. In this limit, the term in square brackets of eq B.20 approaches 1. Thus, the relationship between the polarization parameters $\mathscr{A}_q^{(k)}$ and the polarization parameters $a_q^{(k)}$ may be determined:

$$\mathscr{A}_q^{(k)} = (\delta_{k2}+1)(\lim_{J'\to\infty}c(k,J'))\frac{1}{(J'(J'+1))^{k/2}}\langle J_q^{(k)}\rangle$$
$$= (\delta_{k2}+1)\left(\frac{(2k-1)!!}{k!}\right)^{1/2}\frac{1}{(J'(J'+1))^{k/2}}\langle J_q^{(k)}\rangle$$
$$= (\delta_{k2}+1)\left[\frac{(2J'+1+k)!}{(2J'+1)!2^k(J'(J'+1))^{k/2}}\right]a_q^{(k)} \quad (B.18)$$

The factor of $\delta_{k2}+1$ in eq B.18 is equal to 1 when $k \neq 2$ and 2 when $k = 2$. The confusion this factor causes is an unfortunate legacy of the history of alignment parameters.

From the form of eq B.15, we see that the polarization parameters vanish when $k > 2J'$ or $|q| > k$. Thus, just as there are $(2J'+1)^2$ elements in the density matrix, there are $(2J'+1)^2$ polarization parameters. Actually, either the polarization parameters or the density matrix may be used to describe the alignment of an ensemble of molecules in a state J'. In contrast to the often opaque physical meaning of individual elements of the density matrix, the polarization parameters of a system are the coefficients of the probability $P(\cos\theta_{J'},\phi_{J'})$ expanded in terms of spherical harmonics. Thus, the $a_0^{(0)}$ moment is proportional to the total population and the $a_0^{(1)}$ moment is proportional to the dipole moment of an ensemble of molecules in a state J'.

The polarization of the $AB(v',J')$ product as a function of scattering angle may be described by a scattering-angle-dependent density matrix.[27] The physical and mathematical properties of the polarization parameters make it advantageous, however, to describe the vector correlations that occur in a photoloc experiment by the polarization-dependent differential cross sections, $d\sigma_{kq}/d\Omega_r$.

Appendix C. Relationship between the Polarization-Dependent Velocity Distribution $f_{kq}^{ab}(v_{AB})$ and the Polarization-Dependent Differential Cross Section $d\sigma_{kq}/d\Omega_r$

To relate the polarization-dependent differential cross section to the polarization-dependent velocity distribution, we first

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consider only those reactions for which the velocity of the center of mass is fixed to a single value $\mathbf{u}'$. We then convolute the resulting polarization-dependent velocity distribution, $h_{kq}(\mathbf{u}'_{AB} = \mathbf{v}_{AB} - \mathbf{u}')$, over all possible values of $\mathbf{u}'$.

The speed dependence of the velocity distribution $h_{kq}(\mathbf{u}'_{AB})$ is given by a delta function that fulfills the requirement of eq 10. The angular dependence of this distribution is given by the polarization-dependent differential cross section. Thus, we have

$$h_{kq}(\mathbf{u}'_{AB}) = \frac{\delta(u'_{AB} - u_{AB})}{u^2_{AB}}\left(\frac{1}{\sigma}\frac{d\sigma_{kq}}{d\Omega_r}\right) \quad (C.1)$$

where u_{AB} is the constant given in eq 10. To calculate the spherical tensor density $f_{kq}(\mathbf{v}_{AB})$, we need to find the average of the polarization described by $h_{kq}(\mathbf{u}'_{AB} = \mathbf{v}_{AB} - \mathbf{u}')$ when weighted by the distribution $g(\mathbf{u}')$ of center-of-mass velocities where

$$g(\mathbf{u}') = \frac{\delta(u' - u)}{4\pi u^2}(1 + \beta_{phot}P_2(\hat{\boldsymbol{\epsilon}}\cdot\hat{\mathbf{u}}')) \quad (C.2)$$

Here, u is the constant given by eq 9 and $P_2(x) = (3x^2 - 1)/2$ is the second Legendre polynomial. Care must be taken before convoluting $h_{kq}(\mathbf{u}'_{AB})$ with the distribution of center-of-mass velocities. If we wish to calculate the average of several polarization parameters, we must express each parameter with respect to the same frame of reference. Similarly, before convoluting $h_{kq}(\mathbf{u}'_{AB})$ with $g(\mathbf{u}')$, we need to rotate $h_{kq}(\mathbf{u}'_{AB})$ to a frame of reference that is independent of the variable of integration, $\mathbf{u}'$. For this purpose, we rotate the polarization parameters to the laboratory frame shown in Figure 1c. If the velocity of the center of mass of a scattering event is given by the laboratory-frame coordinates $\mathbf{u}' = (u', \theta'^{lab}_u, \phi'^{lab}_u)$, then the scattering frame of the reaction is transformed to the laboratory frame by rotation through the Euler angles $\theta_R = 0$, $\phi_R = 0$, and $\chi_R = \pi - \phi'^{lab}_u$ (Figure 1c). The polarization-dependent distribution of $\mathbf{v}_{AB}$ measured in the laboratory frame, $f_{kq}(\mathbf{v}_{AB})$, is given by the convolution integral

$$f^{lab}_{kq}(\mathbf{v}_{AB}) = \int d\mathbf{u}'\, g(\mathbf{u}')\sum_{q'}D^k_{q'q}(\phi_R = 0, \theta_R = 0,$$

$$\chi_R = \pi - \phi'^{lab}_u)h_{kq'}(\mathbf{v}_{AB} - \mathbf{u}') \quad (C.3)$$

where $D^k_{q'q}(\theta_R,\phi_R,\chi_R)$ is a Wigner rotation matrix. The integral of eq C.3 is straightforward when the following substitutions are made[13]

$$g(\mathbf{u}') = \frac{\delta(u' - u)}{4\pi u^2}\left[1 + \frac{4\pi\beta}{5}\sum_{m=-2}^{2}Y^*_{2m}(\theta'^{lab}_u,\phi'^{lab}_u)Y_{2m}(\theta_\epsilon,0)\right] \quad (C.4)$$

and

$$h_{kq}(\mathbf{v}_{AB} - \mathbf{u}') =$$

$$\left(\frac{1}{u'v_{AB}u_{AB}}\right)\left(\frac{1}{\sigma}\frac{d\sigma_{kq}}{d\Omega_r}\right)\delta\left(\frac{v^2_{AB} + u'^2 - u^2_{AB}}{2u'v_{AB}} - \cos\theta'^{lab}_u\right) \quad (C.5)$$

where the cross section is evaluated at the scattering angle given by eq 13. The solution to the integral of eq C.3 is given by eqs 37-41.

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