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Vector Correlation Analysis for Inelastic and Reactive Collisions between Partners Possessing Spin and Orbital Angular Momentum[†]

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A general reactive collision of the type A + B → C + D is considered where both the collision partners (A and B) or the products (C and D) may possess internal, i.e., spin, orbital or rotational, angular momenta. Compact expressions are derived using a rigorous quantum mechanical analysis for the angular momentum anisotropy of either of the products (C or D) arising from an initially polarized distribution of the reactant angular momentum. The angular momentum distribution of the product is expressed in terms of canonical spherical tensors multiplied by anisotropy-transforming coefficients $\mathbf{c}^{K}_{K_i q_k}(K_r,L)$. These coefficients act as transformation coefficients between the angular momentum anisotropy of the reactants and that of the product. They are independent of scattering angle but depend on the details of the scattering dynamics. The relationship between the coefficients $\mathbf{c}^{K}_{K_i q_k}(K_r,L)$ and the body-fixed scattering **S** matrix is given and the methodology for the quantum mechanical calculation of the anisotropy-transforming coefficients is clearly laid out. The anisotropy-transforming coefficients are amenable to direct experimental measurement in a similar manner to vector correlation and alignment parameters in photodissociation processes. A key aspect of the theory is the use of projections of both reactant and product angular momenta onto the product recoil vector direction. An important new conservation rule is revealed through the analysis, namely that if the state multipole for reactant angular momentum distribution has a projection q_k onto the product recoil vector the state multipoles for the product angular momentum distribution all have this same projection. Expressions are also presented for the distribution of the product angular momentum when its components are evaluated relative to the space-fixed Z-axis. Notes with detailed derivations of all the formulas are available as Supporting Information.

I. Introduction

Stimulated by the pioneering works of Fano and Macek[1] and of Herschbach and co-workers,[2,3] the field of stereodynamics and vector correlation in inelastic and reactive molecular collisions dynamics has attracted much attention over recent decades. This has resulted in a very large number of publications; see refs 4−29 and references therein. The importance of vector properties in molecular collision dynamics is a consequence of the fact that practically all interactions within a reaction or collision complex are intrinsically anisotropic and this fact often results in electronic or rotational anisotropy in the reaction products. The form and degree of this anisotropy will normally depend on the direction of scattering; i.e., there will be a correlation between the product recoil vector and the direction of the electronic or rotational angular momentum.

Several different theoretical approaches have been proposed and used in recent years to study the stereodynamical effects discussed above. Some of them[30−32] are based on a semiclassical bipolar moment expansion formalism proposed originally by Dixon[33] for the description of vector correlations in molecular photodissociation. Another approach suggested by Shafer, Orr-Ewing, and Zare[21,34,35] employs a spherical harmonic expansion of the angular momentum distribution in terms of polarization dependent differential cross sections in the center-of-mass reference frame. The quantum mechanical methods using density matrix techniques have been developed by Case and Herschbach[2] and by de Miranda and Clary.[36]

In this paper we consider a general bimolecular reaction of the form:

$$A(j_A) + B(j_B) \rightarrow C(j_C) + D(j_D) \tag{1}$$

where both the reactants and the products may possess polarized internal angular momenta, such as spin, electronic orbital, or rotational angular momentum. Clearly eq 1 includes the possibility of an inelastic nonreactive collision as well. The work described in the present paper presents an alternative treatment to that given by de Miranda and Clary[36,37] and introduces to the field of reactive scattering anisotropy-transforming coefficients similar to those already in use in molecular photodissociation.[38,39]

A density matrix formulation[40] combined with a spherical tensor analysis[41,42] is used to describe the polarization of the reactants. The scattering process is treated quantum mechanically and an explicit relationship is derived between the initial-reagent polarization and final scattering angle dependent product polarizations. Both the initial polarization and the final scattering angle dependent product polarizations are described using spherical tensors and state multipoles.[40,41]

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We present universally valid expressions for the recoil-angle distribution of the state multipole moments for the polarization of one of the products (C) averaged over the quantum states of the other product (D). The most transparent form of the expressions in obtained for the case where the projection axis for the components of the product angular momentum is taken to be the product recoil direction. Expressions are also presented for the case when components of the product angular momentum is referred to space-fixed laboratory axes and simple relationships are presented connecting the two cases.

The scattering angle dependent product angular momentum distribution is written in terms of an expansion over spherical tensors made up from a convolution of standard angular functions and the state multipole of the reactant angular momentum polarization density matrix. The angle-independent coefficients in this expansion, $\mathbf{c}^K_{K_i q_k}(K_r,L)$, contain all the dynamical information associated with the scattering process. We derive expressions for these anisotropy-transforming coefficients in terms of standard scattering $\mathbf{S}$ matrices. Our analysis exposes a new conservation law, namely that the component q_k of the product state multipole of rank K referred to the product recoil vector is conserved in the expansion over the spherical tensors created from a convolution of the reactant state multipole and spherical harmonics of the angle of the initial relative momentum vector of the approach of the two collision partners with respect to the product recoil direction. Stated differently, the projection quantum numbers q_k are constant throughout and the summations involved in the expansion are only over the associated rank, K_i of the spherical tensor.

We also present expressions for state multipoles of the product angular momentum polarization density matrix referred to space-fixed axes. Standard experimental techniques, widely used in photodissociation experiments,[43] can be used to determine the coefficients in this expansion. The expansion itself involves summations over more quantum numbers than the expansion referred to the product recoil direction, but interestingly, the expansion coefficients remain exactly the same but are now multiplied by two standard angular functions.

Several important specific cases of the product polarization distribution are discussed. In particular, reaction between unpolarized particles A and B; reaction between polarized reactants under bulk conditions and the general case of reaction between polarized reactants in a crossed molecular beam apparatus.

Section II presents the general theory, a discussion of the equations and of some special cases is given in section III and some conclusions are given in section IV. Appendices A and B present some details of the derivation of the formulas presented in the paper. An extended detailed derivation of all the formulas in the paper is available in the Supporting Information.

II. General Theory

We consider an inelastic, or a reactive collision of the form of eq 1, where the total “internal” angular momenta of the collision partners or products are $\mathbf{j}_A$, $\mathbf{j}_B$, $\mathbf{j}_C$, and $\mathbf{j}_D$ and the quantum numbers for their projections onto the laboratory Z-axis are m_A, m_B, m_C, and m_D, respectively. The angular momenta may arise from nuclear motion, i.e., rotation, or may be electronic in origin, i.e., spin or orbital electonic angular momentum. The total internal reagent and product angular momenta are $\mathbf{j}_r = \mathbf{j}_A + \mathbf{j}_B$ and $\mathbf{j} = \mathbf{j}_C + \mathbf{j}_D$, respectively.

In the asymptotic region, the scattering wave function in the center of mass reference frame, $\Psi_{n_r}(E,\mathbf{k}_r,\mathbf{k})$, obeys boundary conditions corresponding to an incident plane wave for the relative motion and an internal quantum state $|n_r\rangle$ in the reactant channel and outgoing spherical waves in all product channels associated with internal quantum states $|n\rangle$.[44−48]

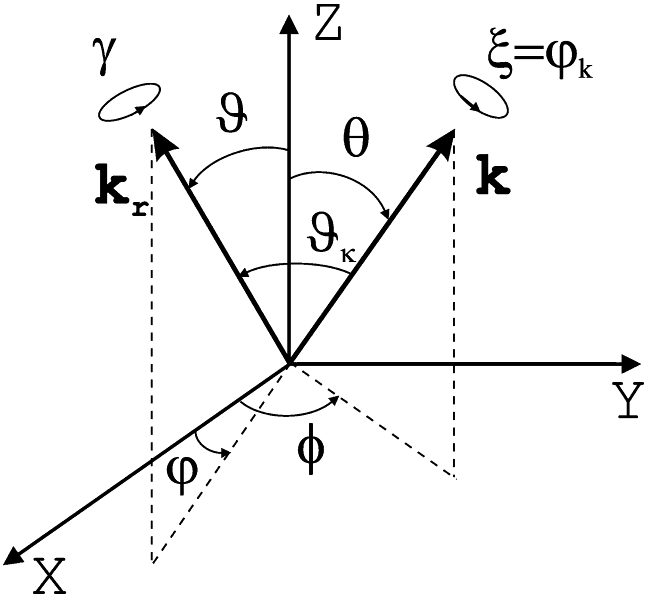

Figure 1. Coordinate reference frames used: (i) X, Y, Z is the laboratory frame, (ii) the Euler angles ϕ, θ, ξ describe the product reference frame where the z-axis is parallel to the recoil wave vector $\mathbf{k}$, (iii) the Euler angles φ, ϑ, γ describe the reactant reference frame where the z'-axis is parallel to the incident relative wave vector of the reactants $\mathbf{k}_r$, (iv) the angles φ_k, ϑ_k describe the direction of the reactant relative wave vector $\mathbf{k}_r$ in the product frame.

$$\Psi_{n_r}(E,\mathbf{k}_r,\mathbf{k}) \overset{R\to\infty}{\sim} e^{i\mathbf{k}_r\cdot\mathbf{R}}|n_r\rangle + \sum_n f_{n,n_r}(E,\mathbf{k}_r,\mathbf{k})\frac{e^{ikR}}{R}|n\rangle \qquad (2)$$

where $\mathbf{k}_r$ and $\mathbf{k}$ are the wave vectors for relative motion in the reactant and product channels respectively, E is the total energy, $k \equiv k^{CD} = [2\mu(E - E_n)]^{1/2}$, μ_r and μ are the corresponding reduced masses, n_r and n are the sets of all quantum number describing the reagent and product states, and R is the interparticle distance before and after the reaction.

In the helicity representation $n_r = v_r, j_r, \Omega_r$ and $n = v, j, \Omega$, where Ω_r and Ω are the projections of the total internal angular momenta $\mathbf{j}_r$ and $\mathbf{j}$ onto the directions $\mathbf{k}_r$ and $\mathbf{k}$, respectively. The indices v_r and v are the sets of all additional quantum numbers that depend on the details of the structure of the reactants and products.

The coordinate reference frames used in this paper are shown in Figure 1. The Euler angles $(\varphi,\vartheta,\gamma)$ specify the reactant reference frame (z'-axis is parallel to the vector $\mathbf{k}_r$), the Euler angles (ϕ,θ,ξ) specify the product reference frame (z-axis is parallel to the vector $\mathbf{k}$) with respect to the laboratory frame XYZ. The polar angles (φ_k,ϑ_k) specify the direction of the reactant relative wave vector, $\mathbf{k}_r$, in the product reference frame.

The scattering wave function $\Psi_{n_r}(E,\mathbf{k}_r,\mathbf{k})$ in eq 2 depends on two vectors, $\mathbf{k}_r$ and $\mathbf{k}$, and can be expanded at all internuclear distances R over products of Wigner $\mathbf{D}$ matrices.[47,49] In the total angular momentum representation the scattering amplitude $f_{vj\Omega;v_rj_r\Omega_r}(\mathbf{k}_r,\mathbf{k})$ in eq 2 can be written as (see Appendix A):

$$f_{vj\Omega;v_r j_r\Omega_r}(\mathbf{k}_r,\mathbf{k}) = \frac{i}{2\sqrt{k^{AB}_{v_r j_r} k^{CD}_{vj}}}\sum_{J,M}(2J+1)\mathbf{D}^{J}_{M\Omega_r}(\varphi,\vartheta,\gamma)\,\mathbf{D}^{J}_{M\Omega}{}^{*}(\phi,\theta,\xi)T^{J}_{vj\Omega;v_r j_r\Omega_r} \tag{3}$$

where J and M are the quantum numbers for the total angular momentum and its projection onto the laboratory frame Z-axis, $\mathbf{D}^{J}_{M\Omega_r}(\varphi,\vartheta,\gamma)$ is a Wigner **D** matrix, and $\mathbf{T}^{J}_{vj\Omega;v_r j_r\Omega_r}$ is the scattering **T** matrix in the total angular momentum representation. The dependence of the scattering amplitude on E in eq 3 has been dropped for brevity.

For a reactive collision, where the nature of the collision partners is changed by the scattering process, the boundary conditions for the scattering wave function in eq 2 should be modified because the inter-reagent distance R in the first term differs in this case from the interproduct distance R' in the second term.[46] The scattering amplitude, $f_{vj\Omega;v_r j_r\Omega_r}(\mathbf{k}_r,\mathbf{k})$, however, may always be correctly expressed as an expansion over products of two Wigner D matrices as shown in eq 3.

The differential reactive cross section is given by[46]

$$\sigma_{vj\Omega,v_r j_r\Omega_r}(\mathbf{k}_r,\mathbf{k}) = \left(\frac{\mu_r k^{CD}}{\mu k^{AB}_r}\right)|f_{vj\Omega;v_r j_r\Omega_r}(\mathbf{k}_r,\mathbf{k})|^2 \tag{4}$$

In keeping with past approaches, we can define a generalized cross section as

$$\sigma_{v'j'\Omega',vj\Omega;\, v_r' j_r'\Omega_r',v_r j_r\Omega_r}(\mathbf{k}_r,\mathbf{k}) = \left(\frac{\mu_r}{\mu}\right)\left(\frac{k^{CD}_{vj}k^{CD}_{v'j'}}{k^{AB}_{v_r j_r}k^{AB}_{v_r' j_r'}}\right)^{1/2} f^{*}_{vj\Omega;v_r j_r\Omega_r}(\mathbf{k}_r,\mathbf{k})\, f_{v'j'\Omega';v_r' j_r'\Omega_r'}(\mathbf{k}_r,\mathbf{k}) \tag{5}$$

The generalized differential cross section in eq 5 describes the probability of detecting the reaction products C and D in their coherent quantum states n, n' arising from a coherent distribution of reactant states n_r, n_r', including all coincidence effects.[40] We have been careful to define the generalized cross section so that primed and unprimed variables appear in a symmetric manner. The "diagonal" terms of the generalized cross section ($\sigma_{vj\Omega,vj\Omega;v_r j_r\Omega_r,v_r j_r\Omega_r}(\mathbf{k}_r,\mathbf{k})$) yield, as expected, the standard differential cross section of eq 4.

The total reagent angular momentum $\mathbf{j}_r$ may be polarized. This means that its magnetic sublevels, labeled by m_r in the space-fixed coordinate system, may be unequally populated. We will describe this polarization using the laboratory frame reagent density matrix,[40,50] $\rho_{j_r' m_r' j_r m_r}$, where in general $j_r' \neq j_r$ and $m_r' \neq m_r$. In the present paper we will not consider the correlation between different j_r rotational levels of the reactants and therefore assume that $j_r = j_r'$. Though the j_r, j_r' coherence may become important if, for instance, the initial reagent polarization is produced by a short laser pulse. The reaction cross section resulting from an initially polarized state of the reactants is obtained by averaging of the generalized reaction cross section in eq 5 over the reagent quantum numbers m_r, m_r' as follows:

$$\sigma_{v'j'\Omega',vj\Omega}(\mathbf{k}_r,\mathbf{k}) = \sum_{m_r,m_r'}\rho_{j_r m_r j_r m_r'}\sigma_{v'j'\Omega',vj\Omega;v_r j_r m_r',v_r j_r m_r}(\mathbf{k}_r,\mathbf{k}) \tag{6}$$

Note that the cross section in the right-hand side of eq 6 has been partially transformed from the reactant coordinate helicity representation in which the angular momentum projections are taken onto the vector $\mathbf{k}_r$ in Figure 1 and are denoted by Ω_r to a space-fixed representation. This transformation involves two Wigner **D** matrices and the associated summations. Full details of the transformation are given in the notes deposited as Supporting Information.

In this paper we use the irreducible representation of the density matrix and express the elements of the reagent density matrix in terms of the *covariant* state multipole moments $\rho^{(j_r)}_{K_r Q_r}$ which are defined as[50]

$$\rho^{(j_r)}_{K_r Q_r} = \sum_{m_r',m_r}(-1)^{j_r-m_r}(2K_r+1)^{1/2}\begin{pmatrix} j_r & j_r & K_r \\ m_r & -m_r' & -Q_r \end{pmatrix}\rho_{j_r m_r' j_r m_r} \tag{7}$$

where K_r and Q_r are the reagent state multipole rank and its projection onto the direction of the laboratory Z-axis, respectively.

The experiments often involve the detection of only one of the reaction products and therefore do not yield simultaneous vector correlation information concerning both of them. The corresponding cross section involves averaging over the quantum numbers of the nondetected reaction product. This averaging is performed by taking the trace of the generalized cross section in eq 6 over the quantum numbers v_D, j_D, and Ω_D that are not actually measured:

$$\sigma^{(j_c)}_{\Omega_c',\Omega_c}(\mathbf{k}_r,\mathbf{k}) = \sum_{v_D,j_D,\Omega_D}\sum_{j',\Omega'}\sum_{j,\Omega} C^{j'\Omega'}_{j_C\Omega_C' j_D\Omega_D} C^{j\Omega}_{j_C\Omega_C j_D\Omega_D}\sigma_{v'j'\Omega',vj\Omega}(\mathbf{k}_r,\mathbf{k}) \tag{8}$$

where $C^{j\Omega}_{j_C\Omega_C j_D\Omega_D}$ is a Clebsch−Gordan coefficient and Ω_C,Ω_C' are projections of the angular momenta $\mathbf{j}_C$, $\mathbf{j}_C'$ onto the product recoil direction $\mathbf{k}$. We have omitted the quantum numbers v and v' from the left-hand side of eq 8 for compactness of notation.

We assume in eq 8 that the product C is detected in a definite quantum state characterized by the quantum numbers v_C and j_C but that the product D is not detected, and we therefore sum over all its possible states.

Note that only the averaging over the helicity quantum number Ω_D in eq 8 is important for the results presented below. One may skip the summation over the quantum numbers v_D and j_D in eq 8 and consider the case when the product D is detected in a quantum state $|v_D,j_D\rangle$; however, no information on the angular momentum polarization of this product is available.

The diagonal ($\Omega_C' = \Omega_C$) elements of the generlaized cross section $\sigma^{(j_c)}_{\Omega_c',\Omega_c}(\mathbf{k}_r,\mathbf{k})$ give the probability of producing the reaction product with a specific value of the fragment angular momenta and its $\mathbf{k}$-component Ω_C, while the off-diagonal elements ($\Omega_C \neq \Omega_C'$) describe the coherence between these states.[40,41]

We now express the elements of the generalized differential cross section $\sigma^{(j_c)}_{\Omega_c',\Omega_c}(\mathbf{k}_r,\mathbf{k})$ in terms of state multipole moments,[40] which are spherical tensors with the rank K and projection q_k onto the product recoil vector $\mathbf{k}$ using the formula:[43]

$$\rho^{(j_C)}_{Kq_k}(\mathbf{k}_r,\mathbf{k}) = \frac{1}{(2j_C+1)^{1/2}\sigma_0} \times \sum_{\Omega'_C,\Omega_C} (-1)^{j_C-\Omega_C}(2K+1)^{1/2} \times \begin{pmatrix} j_C & j_C & K \\ \Omega_C & -\Omega'_C & -q_k \end{pmatrix} \sigma^{j_c}_{\Omega'_C,\Omega_C}(\mathbf{k}_r,\mathbf{k}) \quad (9)$$

where the factor in the brackets is a 3j-symbol,[42] $\sigma_0 = (2j_C+1)^{-1/2}\langle \mathrm{Tr}[\sigma^{(j_C)}(\mathbf{k}_r,\mathbf{k})]\rangle$ is the total reaction cross section calculated for the case of unpolarized reactants, $\rho_{j'_rm'_rj_rm_r} = \delta_{j_rj'_r}\,\delta_{m_r,m'_r}$, and the angular brackets indicate integration over the recoil angles θ,ϕ. The explicit expression for the total reaction cross section σ_0 is given in Appendix B, eq B3.

The product state multipole rank, K, in eq 9 is an integer number and ranges in the interval $0 \le K \le 2j_C$. The quantum number for its projection, q_k, on the product recoil vector takes on values over the range $-K \le q_k \le K$. Due to the symmetry properties of the 3j-symbol, the projection q_k is equal to $q_k = \Omega_C - \Omega'_C$.

The state multipole moments $\rho^{(j_C)}_{Kq_k}(\mathbf{k}_r,\mathbf{k})$ in eq 9 have clear physical meanings. In particular, the state multipole moment with $K = q_k = 0$ is proportional to the conventional differential reaction cross section:

$$\rho^{(j_C)}_{00}(\mathbf{k}_r,\mathbf{k}) = \frac{1}{(2j_C+1)\sigma_0}\sum_{\Omega_C}\sigma^{j_C}_{\Omega_C,\Omega_C}(\mathbf{k}_r,\mathbf{k}) \quad (10)$$

while all multipole moments with $K > 0$ refer to the product angular momentum distribution.

In the product recoil frame used in eq 9, the z-axis is parallel to the product recoil wave vector $\mathbf{k}$. It can be shown[40] that the $q_k = 0$ component of the state multipole moment $\rho^{(j_C)}_{K0}$ with rank K is proportional to the mean value of the Kth power of the z-component of the angular momentum $\mathbf{j}_C$. In particular for $K = 1, 2$,

$$\rho^{(j_C)}_{10} = \left(\frac{3}{j_C(j_C+1)(2j_C+1)}\right)^{1/2}\langle (j_C)_z\rangle \quad (11)$$

$$\rho^{(j_C)}_{20} = \left(\frac{5}{j_C(j_C+1)(2j_C-1)(2j_C+1)(2j_C+3)}\right)^{1/2}\langle 3(j_C)_z^{\ 2} - \mathbf{j}_C^{\ 2}\rangle \quad (12)$$

Equations 11 and 12 refer to the angular momentum distributions which are axially symmetric with respect to the z-axis. In contrast, the expressions for the $q_k \neq 0$ components of the state multipole moment $\rho^{(j_C)}_{Kq_k}$ contain the mean values of the powers of the x and y-components of the angular momentum $\mathbf{j}_C$ and refer to the angular momentum distributions which are not axially symmetric with respect to the z-axis.

The equations presented so far, eqs 3 and 5 have been written in terms of a standard helicity representation in which the reactant angular momenta are referred to the reactant relative momentum vector, $\mathbf{k}_r$, and the angular momenta of the products are referred to the product recoil vector $\mathbf{k}$. The principal novel idea of the ensuing derivation is that *all* angular momenta involved in the problem will be referred to the *direction of the product recoil vector* $\mathbf{k}$. We call this the product reference (PR) frame. The laboratory frame reagent state multipole moment of eq 7 is expressed in the PR frame as[42]

$$\rho^{(j_r)}_{K_rq_r} = \sum_{Q_r}\rho^{(j_r)}_{K_rQ_r}\mathbf{D}^{K_r}_{Q_rq_r}(\phi,\theta,\xi) \quad (13)$$

where q_r is the projection of the rank K_r onto the direction of the product recoil wave vector $\mathbf{k}$. As will be shown below, the angle ξ in eq 13 can be set to zero without any loss of generality (see a comment after eq 20).

Starting from eqs 5, 8, and 9 we show in Appendix B (and in greater detail in notes deposited as Supporting Information) that the product C state multipole moments can be presented in the PR frame in the following compact form:

$$\rho^{(j_C)}_{Kq_k} = N\sum_{K_i}\sum_{L,K_r}\mathbf{c}^K_{K_iq_k}(K_r,L)\,\mathscr{R}^{K_rL}_{K_iq_k}(\vartheta_k,\varphi_k) \quad (14)$$

where q_k ($=q_i$) is the projection of both the ranks K and K_i onto the product recoil vector $\mathbf{k}$.

All indices in eq 14 have clear physical meaning. In particular, the rank L is associated with the angular momentum arising from the relative motion of the reactants, the rank K_r is associated with the polarization of the total angular momentum of the reactants $\mathbf{j}_r$, the rank K_i describes the total reagent anisotropy (arising from the coupling of L and K_r; see Appendix B eq B6), and the rank K describes the polarization of the product angular momentum $\mathbf{j}_C$.

The spherical tensor $\mathscr{R}^{K_rL}_{K_iq_i}(\vartheta_k,\varphi_k)$ in eq 14 with the rank K_i and projection q_i describes the initial anisotropy of the particles A and B before the reaction. It is given as an irreducible product of the spherical harmonic $Y_{Lq_l}(\vartheta_k,\varphi_k)$ and the reagent state multipole moment $\rho^{(j_r)}_{K_rq_r}$ in eq 13:

$$\mathscr{R}^{K_rL}_{K_iq_i}(\vartheta_k,\varphi_k) = \sum_{q_l,q_r} C^{K_iq_i}_{Lq_lK_rq_r}Y_{Lq_l}(\vartheta_k,\varphi_k)\rho^{(j_r)}_{K_rq_r} \quad (15)$$

where $C^{K_iq_i}_{Lq_lK_rq_r}$ is a Clebsch–Gordan coefficient and the spherical angles (ϑ_k, φ_k) specify the direction of the wave vector of the relative motion of the reactants $\mathbf{k}_r$ in the PR reference frame; see Figure 1.

Using eq 13, the spherical tensor $\mathscr{R}^{K_rL}_{K_iq_i}(\vartheta_k,\varphi_k)$ in eq 15 can be written as an explicit function of two pairs of the polar angles ϑ_k, φ_k and θ, ϕ. As can be shown, the tensors $\mathscr{R}^{K_rL}_{K_iq_i}(\vartheta_k,\varphi_k)$ are orthogonal as a function of the polar angles (ϑ_k, φ_k) and (θ, ϕ) over the indices K_i, q_i, and K_r, L. Therefore, the expansion coefficients $\mathbf{c}^K_{K_iq_k}(K_r,L)$ in eq 14 are scalar quantities defined as

$$\mathbf{c}^K_{K_iq_k}(K_r,L) = N^{-1}\frac{\langle\langle \rho^{j_C}_{Kq_k}\mathscr{R}^{K_rL*}_{K_iq_i}\rangle\rangle}{\langle\langle \mathscr{R}^{K_rL}_{K_iq_k}\mathscr{R}^{K_rL*}_{K_iq_i}\rangle\rangle} \quad (16)$$

where the double angular brackets signify integration over all angles.

The proportionality constant N in eq 14 can be chosen as

$$N = \frac{\sqrt{2j_r+1}}{\sqrt{4\pi(2j_C+1)}} \quad (17)$$

providing the normalization conditions: $\mathbf{c}^0_{00}(0,0) = 1$ and $\langle\rho^{(j_C)}_{00}\rangle = 1/[2j_C+1]^{1/2}$. The explicit expression for the coefficients

$\mathbf{c}^{K}_{K_iq_k}(K_\mathrm{r},L)$ in terms of the quantum scattering matrix is given in eq B6 of Appendix B.

No simplifying assumptions have been used in derivation of eqs 14−16 or the equations of Appendix B, they depend only on the explicit form of the scattering amplitude in eq 3 and on the symmetry of the spherical tensors under rotation of the coordinate systems.

Equation 14 makes explicit that the quantum numbers q_k and q_i are equal to each other. They can take the values $q_k = q_i = 0, \pm1, \pm2, ...$, as long as $|q_k| \le |K|$ and $|q_i| \le |K_i|$. From eq 15 we see that $q_i = q_\mathrm{r} + q_l$ arises from a coupling of the reactant polarization and the relative motion of the reactants. But the Clebsch−Gordan coefficient $C^{j'\Omega'}_{j\Omega K-q_k}$ in eq B4 also shows that $q_k = \Omega-\Omega'$, where Ω and Ω' are helicity quantum numbers related to the polarization of the products. *The quantum number* $q_k = q_i$ *is therefore related to the polarization of both the reactants and the products and is conserved throughout the reaction.* The conservation of q_k shows up through the fact that the spherical tensors of the rank K in the right and left-hand sides of eq 14 transform in the same way under rotation about the vector **k** (i.e., the z-component of the rank, q_k, is conserved throughout).

Conservation of the quantum number q_k is an important new selection rule which is valid when the differential cross section is averaged over the helicity quantum numbers Ω_D of the second (undetected) product, as shown in eq 8. This selection rule underlies the polarization and coherence effects of the product angular momentum in inelastic and reactive collisions.[43] It is worth while noting that neither the reagent and product angular momenta j_r and j nor their helicity projections Ω_r and Ω in eq 3 are in general preserved in the reaction 1.

Transforming the spherical harmonics $Y_{Lq_l}(\vartheta_k,\varphi_k)$ in eq 15 to the laboratory reference frame:

$$Y_{Lq_l}(\vartheta_k,\varphi_k) = \sum_{Q_L} Y_{LQ_L}(\vartheta,\varphi)\, \mathbf{D}^{L}_{Q_Lq_l}(\phi,\theta,\xi) \tag{18}$$

using eq 13, and applying the Clebsch−Gordan series,[42] the state multipole angular distribution in eq 14 can be written in the laboratory frame where all angular momenta are projected onto the laboratory Z-axis (see Figure 1 and Supporting Information):

$$\rho^{(j_\mathrm{C})}_{KQ} = N \sum_{K_i,q_k,Q_i} \sum_{L,K_\mathrm{r}} \mathbf{c}^{K}_{K_iq_k}(K_r,L)\, \mathbf{D}^{K}_{Qq_k}{}^{*}(\phi,\theta,\xi)\, \mathbf{D}^{K_i}_{Q_iq_k}(\phi,\theta,\xi)\, \mathscr{R}^{K_\mathrm{r}L}_{K_iQ_i}(\vartheta,\varphi) \tag{19}$$

where the spherical tensor $\mathscr{R}^{K_\mathrm{r}L}_{K_iQ_i}(\vartheta,\varphi)$ in the laboratory frame is given by

$$\mathscr{R}^{K_\mathrm{r}L}_{K_iQ_i}(\vartheta,\varphi) = \sum_{Q_L,Q_\mathrm{r}} C^{K_iQ_i}_{LQ_LK_\mathrm{r}Q_\mathrm{r}} Y_{LQ_L}(\vartheta,\varphi)\rho^{(j_\mathrm{r})}_{K_\mathrm{r}Q_\mathrm{r}} \tag{20}$$

where Q, Q_i, Q_r, and Q_L are projections of the corresponding ranks onto the laboratory Z-axis. The left-hand side of eq 19 does not in fact depend on the value of the third Euler angle ξ, which can therefore be set to zero without any loss of generality.

Equations 14−20 represent the main result of this paper. Equation 19 provides a compact and universal expression for the product recoil angle dependence, in the laboratory reference frame, of the polarization of one of the scattered products in an experiment arising from a general polarized angular momentum distribution in the reactants. It is completely general and depends only on the symmetry of the quantum mechanical scattering amplitude and on the properties of spherical tensors irrespectively of the reaction dynamics. Equations 14 and 19 hold in general because any solution of the scattering equations can be presented in the form given in these equations. The equations are fully quantum mechanical and can be used for the description of the angular momentum anisotropy arising in elastic, inelastic, or reactive collisions between atomic, molecular, or nuclear particles possessing any values of their internal angular momenta, including spin.

The spherical tensor in eq 20 is a direct product of the laboratory frame spherical harmonic $Y_{LQ_L}(\vartheta,\varphi)$ and the reagent state multipole moment $\rho^{(j_\mathrm{r})}_{K_\mathrm{r}Q_\mathrm{r}}$. $Y_{LQ_L}(\vartheta,\varphi)$ describes the anisotropy caused by the relative motion of the reactants, while $\rho^{(j_\mathrm{r})}_{K_\mathrm{r}Q_\mathrm{r}}$ describes the anisotropy caused by the polarization of the "internal" reagent angular momentum $\mathbf{j}_\mathrm{r}$.

The expansion coefficients $\mathbf{c}^{K}_{K_iq_k}(K_\mathrm{r},L)$ in eqs 14 and 19 can be used as a set of the universal anisotropy transforming parameters to describe the collisional dynamics. The parameters do not depend on any angles nor on any experimental details or methods used. They contain all information about the body-frame molecular dynamics of the collision or reaction process and are based on rigorous quantum mechanical theory. The coefficients $\mathbf{c}^{K}_{K_iq_k}(K_\mathrm{r},L)$ in eq 14 are the elements of a matrix that performs a transformation between the initial anisotropy of the reagents, described by the spherical tensor $\mathscr{R}^{K_\mathrm{r}L}_{K_iq_k}$, and the anisotropy in the reaction product described by the spherical tensor $\rho^{(j_\mathrm{C})}_{Kq_k}$.

The anisotropy-transforming coefficients $\mathbf{c}^{K}_{K_iq_k}(K_\mathrm{r},L)$ are in general complex (in the mathematical sense). Using the symmetry properties of spherical tensors, we can show from eq 14 that they obey the following relationship:

$$[\mathbf{c}^{K}_{K_iq_k}(K_\mathrm{r},L)]^{*} = \mathbf{c}^{K}_{K_i-q_k}(K_\mathrm{r},L) \tag{21}$$

It follows from eq 21 that the coefficients $\mathbf{c}^{K}_{K_i0}(K_\mathrm{r},L)$ are real.

As has recently been shown by Shternin and Vasyutinskii[39] who considered the photolysis of an isotropic ensemble of molecules, the fragment state multipoles in the recoil and laboratory reference frames can also be represented in forms similar to those in eqs 14 and 19. In this case $K_\mathrm{r} = 0$ and the spherical harmonics describing the relative motion of the reaction reagents, $Y_{Lq_l}(\mathbf{k}_\mathrm{r})$ in eqs 15 and 20, are replaced by the photon polarization matrix $E_{K_\mathrm{ph}q_\mathrm{ph}}(\mathbf{e})$, where $\mathbf{e}$ is the polarization vector of the photolysis light. In the photolysis case, the number of terms in the expansions (14) and (19) is always finite, because the photon rank, K_ph, is limited to the values $K_\mathrm{ph} = 0, 1, 2$.[50] Shternin and Vasyutinskii[39] have shown that, in the case of photolysis, all the anisotropy coefficients $\mathbf{c}^{K}_{K_{ph}q_k}$ are either proportional to other commonly used anisotropy parameters[51] or equal to zero, with $\mathbf{c}^{0}_{00} = -\sqrt{3}$.

Applying the Clebsch−Gordan series[41] to the product of the two Wigner **D** matrices in eq 19, this state multipole angular distribution can be presented in an alternative form:

$$\rho^{(j_\mathrm{C})}_{KQ} = \sqrt{4\pi}N \sum_{K_i,N} \sum_{L,K_\mathrm{r}} (2\Lambda + 1)^{1/2} P^{K}_{\Lambda K_i}(K_\mathrm{r},L) \times [Y_{\Lambda}(\theta,\phi) \otimes \mathscr{R}^{K_\mathrm{r}L}_{K_i}(\vartheta,\varphi)]_{KQ} \tag{22}$$

where the term in the square brackets is a direct product of the spherical harmonic $Y_{\Lambda\lambda}(\theta,\phi)$ and the spherical tensor $\mathcal{R}^{K_rL}_{K_iQ_i}(\vartheta,\varphi)$ in eq 20

$$[Y_{\Lambda}(\theta,\phi) \otimes \mathcal{R}^{K_rL}_{K_i}(\vartheta,\varphi)]_{KQ} = \sum_{\lambda,Q_i} C^{KQ}_{\Lambda\lambda K_iQ_i} Y_{\Lambda\lambda}(\theta,\phi)\, \mathcal{R}^{K_rL}_{K_iQ_i}(\vartheta,\varphi) \tag{23}$$

and $P^K_{\Lambda K_i}(K_r,L)$ is the scalar line strength factor which can be presented in the form:

$$P^K_{\Lambda K_i}(K_r,L) = \sum_{q_k}(-1)^{K-q_k}\frac{\mathbf{c}^K_{K_iq_k}(K_r,L)}{\sqrt{2K+1}}\begin{pmatrix}\Lambda & K_i & K\\ 0 & -q_k & q_k\end{pmatrix} \tag{24}$$

The angular distribution in eq 22 is equivalent to eq 19; however, it is written in a form of an expansion over the spherical harmonics $Y_{\Lambda\lambda}(\theta,\phi)$, rather than of an expansion over the product of two **D**-functions in eq 19. In the case of the expansion in eq 22, the scalar line strength factors $P^K_{\Lambda K_i}(K_r,L)$ in eq 24 are used as basic expansion coefficients instead of the anisotropy-transforming parameters $\mathbf{c}^K_{K_iq_k}(K_r,L)$.

The application of eqs 14 and 19 to the analysis of product state polarization distributions in several different experimental situations is discussed in the next section.

III. Discussion

A. Reaction between Unpolarized Particles.

If the reaction occurs between unpolarized reagents, the reagent total angular momenta $\mathbf{j}_r$ are isotropically distributed in space. In this case the rank K_r in eqs 15 and 14 is equal to zero, $\rho^{(j_r)}_{K_rq_r} \equiv \rho^{(j_r)}_{00} = 1/[2j_r + 1]^{1/2}$, $K_i = L$, and the state multipole moments for the polarization of the product angular momentum in the PR frame, $\rho^{(j_C)}_{Kq_k}$ in eq 14, depend only on the direction of the initial relative reactant wave vector $\mathbf{k}_r(\vartheta_k,\varphi_k)$ in the PR frame; see Figure 1. In this case eq 14 can be written as

$$\rho^{(j_C)}_{Kq_k}(\vartheta_k,\varphi_k) = \frac{1}{\sqrt{4\pi(2j_C+1)}}\sum_L \mathbf{c}^K_{Lq_k}Y_{Lq_k}(\vartheta_k,\varphi_k) \tag{25}$$

where $\mathbf{c}^K_{Lq_k} \equiv \mathbf{c}^K_{Lq_k}(0,L)$ and $\mathbf{c}^0_{00} = 1$.

1. Detection of the Product Distribution. If only the relative number $\mathcal{P}$ of the reaction product is detected, $K = q_k = 0$ and eq 25 describes the $\mathbf{v} - \mathbf{v}$ correlations as in the conventional differential reaction cross section $\mathcal{P} = (2j_C + 1)^{1/2}\rho^{(j_C)}_{00}(\varphi_k,\vartheta_k)$:

$$\mathcal{P} = \frac{1}{\sqrt{4\pi}}\sum_L \mathbf{c}^0_{L0}Y_{L0}(\vartheta_k,\varphi_k) = \frac{1}{4\pi}\sum_L \mathbf{c}^0_{L0}\sqrt{2L+1}P_L(\cos\vartheta_k) \tag{26}$$

As shown in eq 26, the spatial distribution of the reaction products is cylindrically symmetric when viewed in either the reactant or the product reference frames and does not depend on the azimuthal angle φ_k. The distribution in eq 26 is an expansion over the Legendre polynomials $P_L(\cos\vartheta_k)$ of the ranks $L = 0, 1, 2, ...$ The odd-order terms in this expansion describe the forward−backward anisotropy of the differential reaction cross section, while the even-order terms are symmetric with respect to forward−backward scattering and describe the alignment of the scattering along this direction. This type of distribution of the reaction products have been intensively studied both experimentally and theoretically.[52] The corresponding laboratory frame expression is given by eq 19, where $K = K_r = q_k = q_r = 0$:

$$\mathcal{P} = \frac{1}{\sqrt{4\pi}}\sum_{L,Q_L}\mathbf{c}^0_{L0}\mathbf{D}^L_{Q_L0}(\phi,\theta,0)\,Y_{LQ_L}(\vartheta,\varphi) = \sum_{L,Q_L}\mathbf{c}^0_{L0}\frac{Y^*_{LQ_L}(\theta,\phi)\,Y_{LQ_L}(\vartheta,\varphi)}{\sqrt{2L+1}} \tag{27}$$

where the polar angles (θ,ϕ) and (ϑ,φ) specify the directions $\mathbf{k}$ and $\mathbf{k}_r$ in the laboratory frame; see Figure 1. The number of the expansion terms in eqs 26 and 27 is in principle infinite; however, in practice the expansion may be truncated by neglecting the higher order terms, which become less important after some value of L. Also, the angular distribution of the reagent relative velocities $\mathbf{k}_r$ can often be presented as an expansion over a finite number of spherical harmonics, resulting after averaging over the angles φ, ϑ in eq 27 in a finite number of the coefficients $\mathbf{c}^0_{L0}$.

In particular, if the reaction reagents are produced in the photolysis of precursor molecules, the angular distribution of the relative reagent wave vectors $\mathbf{k}_r(\vartheta)$ can be described by the well-known formula[41] $f(\cos\vartheta) \sim 1 + \beta P_2(\cos\vartheta)$. Averaging of the angular distribution in eq 27 over the $f(\cos\vartheta)$ distribution gives the product angular distribution containing only two terms (see ref 53 for an early, slightly approximate, derivation):

$$\langle f\mathcal{P}\rangle = \frac{1}{4\pi}\left[1 + \frac{\mathbf{c}^0_{20}\beta}{\sqrt{5}}P_2(\cos\theta)\right] \tag{28}$$

2. Detection of the Product Angular Momentum Polarization. If the distribution of the reaction products in definite (polarized) quantum states is detected, the product state multipole moments of eq 25 with $K > 0$ describe the $\mathbf{v} - \mathbf{j}$ correlations. The product state multipole moments are in this case proportional to the polarization-dependent differential cross sections, $\sigma^{j_C}_{Kq_k}(\vartheta_k,\varphi_k) \sim \rho^{(j_C)}_{Kq_k}(\vartheta_k,\varphi_k)$.[36] The anisotropy coefficients $\mathbf{c}^K_{Lq_k}$ appearing in the expansion of the product state multipoles (eq 25) provide a convenient measure and codification of the product angular momentum anisotropy. The quantum number L in general ranges from zero to infinity, the rank K ranges from $K = 0$ to $K = 2j_C$, and the projection q_k ranges from $q_k = -\min(L,K)$ to $q_k = \min(L,K)$. The terms in eq 25 with odd values of the rank K describe the *orientation* of the product angular momentum $\mathbf{j}_C$ and the terms with even, nonzero values of the rank K describes the *alignment* of the product angular momentum $\mathbf{j}_C$.

The symmetry of the state multipole moments $\rho^{(j_C)}_{Kq_k}(\vartheta_k,\varphi_k)$ distribution in eq 25 is in general determined by two vectors $\mathbf{k}_r$ and $\mathbf{j}_C$ and depends strongly on the index q_k. If $q_k = \Omega_C - \Omega'_C = 0$, which is associated with the noncoherent product angular momentum distribution, the distribution of the product angular momentum $\mathbf{j}_C$ is symmetric with respect to rotation about the product frame z-axis (the product recoil vector $\mathbf{k}$); see eqs 11 and 12. In these cases, the distribution in eq 25 depends on the polar angle ϑ_k between the directions $\mathbf{k}$ and $\mathbf{k}_r$ but does not depend on the azimuthal angle φ_k. Therefore the $q_k = 0$ state multipole moments $\rho^{(j_C)}_{Kq_k}(\vartheta_k,\varphi_k)$ are always *cylindrically symmetric* about the product recoil vector $\mathbf{k}$.

When $K \neq 0$, $q_k = \Omega_C - \Omega'_C \neq 0$, there is a coherence between Ω_C and Ω'_C helicity states and the angular momentum $\mathbf{j}_C$ is not distributed in a manner which is symmetric with respect to rotation about the product frame z-axis. The product state multipole, or the polarization dependent differential cross section,[36] in eq 25 depends on both the angles ϑ_k and φ_k and therefore breaks the *cylindrical symmetry* about the product recoil vector $\mathbf{k}$.

Note that the necessary procedures for experimentally measuring each of the two types of state multipole moments discussed in this subsection are now well developed and routinely used in photodissociation studies.[38,43] Analogous alignment moments have also been measured for rotationally inelastic scattering.[54]

B. Reaction between Polarized Particles in a Bulk Environment. If the polarization of the total reagent angular momentum $\mathbf{j}_r$ is considered, the rank K_r in eqs 15 and 20 differs from zero, $0 < K_r \leq 2j_r$. Odd values of the rank K_r are responsible for the orientation and even values of rank K_r are responsible for the alignment of the total reagent angular momentum $\mathbf{j}_r$, respectively.

In this section we consider the reaction in the bulk environment, when the distribution of the relative reagent wave vectors $\mathbf{k}_r$ is isotropic. In this case, the rank L in eqs 15 and 20 is equal to zero and the product-frame product angular distribution in eq 14 can be written as

$$\rho_{Kq_k}^{(j_C)} = \frac{N}{\sqrt{4\pi}} \sum_{K_r} \mathbf{c}_{K_r q_k}^{K}(K_r,0) \rho_{K_r q_k}^{(j_r)} \qquad (29)$$

The corresponding laboratory-frame distribution which can be readily obtained from eq 19 is given by

$$\rho_{KQ}^{(j_C)}(\theta,\phi) = \frac{N}{\sqrt{4\pi}} \sum_{q_k} \sum_{K_r,Q_r} \mathbf{c}_{K_r q_k}^{K}(K_r,0)\, \mathbf{D}_{Qq_k}^{K}{}^*(\phi,\theta,0)\, \mathbf{D}_{Q_r q_k}^{K_r}(\phi,\theta,0) \rho_{K_r Q_r}^{(j_r)} \qquad (30)$$

The product state multipole moment distribution in eqs 29 and 30 describes the polarization of the product angular momentum $\mathbf{j}_C$ and depends on the polarization of the reactant angular momentum $\mathbf{j}_r$. The rank K ranges from 0 to $2j_C$, the rank K_r ranges from 0 to $2j_r$, and the projection q_k ranges from $q_k = -\min(K_r,K)$ to $q_k = \min(K_r,K)$. Thus, the total number of the terms in the expansions in eqs 29 and 30 is always finite.

Assuming that the initial distribution of the reagent angular momenta $\mathbf{j}_r$ is symmetric with respect to the laboratory Z-axis, we can hold $Q_r = 0$ in eq 30. Both $Q = 0$ and $Q \neq 0$ components of the product state multipole moments $\rho_{KQ}^{(j_C)}(\phi,\theta)$ can differ from zero in eq 30.

The $Q = 0$ components depend on the polar angle θ but do not depend on the azimuthal angle ϕ, and therefore they describe the distribution of the product angular momentum vectors $\mathbf{j}_C$, which possesses cylindrical symmetry with respect to the direction of the axis Z. Only these components exist if the *number* of reaction products, $\mathscr{P}$, is detected, $K = Q = 0$ and eq 29 describes the $\mathbf{j} - \mathbf{v}$ correlations in the differential reaction cross section $\sigma(\theta,\phi) \sim \mathscr{P} = (2j_C + 1)^{1/2} \rho_{00}^{(j_C)}(\theta,\phi)$.

The $Q \neq 0$ components of the product state multipole moments $\rho_{KQ}^{(j_C)}(\phi,\theta)$ in eq 30 depend of both polar angles θ and ϕ, and therefore they describe the distribution of the vectors $\mathbf{j}_C$ which break the cylindrical symmetry about the axis Z.

C. Reaction between Polarized Particles in the Crossed Molecular Beam Conditions. ***1. Total Reaction Yield.*** When the total reaction yield is detected, eq 19 with $K = Q = 0$ should be integrated over the recoil angles θ and ϕ. The polarization effects in the total cross section in atom−atom inelastic transitions have been experimentally observed by Leone et al.[7,12,13] and Manders et al.[14,15] and interpreted through potential-curve crossing and locking-radius models.[16,17] In this case, eq 19 can be presented in the form

$$\langle \rho_{00}^{(j_C)} \rangle = 4\pi N \sum_{K_r} (-1)^{K_r} \frac{\mathbf{c}_{00}^{0}(K_r,K_r)}{\sqrt{2K_r + 1}} \big(\rho_{K_r}(j_r) \cdot Y_{K_r}(\vartheta,\varphi)\big) \qquad (31)$$

where the term in the parentheses is a tensor scalar product:[42]

$$\big(\rho_{K_r}(j_r) \cdot Y_{K_r}(\vartheta,\varphi)\big) = \sum_{Q_r} \rho_{K_r Q_r}(j_r)\, Y_{K_r Q_r}^{*}(\vartheta,\varphi) \qquad (32)$$

As shown in eq 31, the total reaction yield $\langle \rho_{00}^{(j_C)} \rangle$ depends on the scalar product of a spherical harmonic dependent on the direction of reagent relative wave vector $\mathbf{k}_r$ and the state multipole describing the polarization of the reagent angular momentum $\mathbf{j}_r$. The quantum number K_r in eq 31 is limited to $K_r = 0,..., 2j_r$, and therefore the number of coefficients $\mathbf{c}_{00}^{0}(K_r,K_r) = \mathbf{c}(K_r)$ needed for the complete description of the polarization effects is in general equal to $2j_r + 1$. However, in the case when the reagent angular momentum polarization is prepared by a one-photon laser excitation, $K_r = 0, 1, 2$ and the number of the coefficients is equal to 3.

2. Differential Cross Section of the Reaction Products. In this case, the product polarization rank K and its projections q_k and Q are equal to zero. The zeroth rank PR frame state multipole moment $\rho_{00}^{(j_C)}$ in eq 14 in general depends on the two vectors $\mathbf{k}_r$ and $\mathbf{j}_r$ and its laboratory-frame counterpart in eq 19 depends on the three vectors $\mathbf{k}_r$, $\mathbf{j}_r$, and $\mathbf{k}$. Experimentally, the electronic orbital angular momentum alignment dependence of the reaction differential cross section in cross-beam experiments have been studied for atom−atom collisions by Visticot et al.[19] and for atom−molecule collisions by Suits et al.[18]

In this case $q_i = 0$ and $q_l = -q_r$ in eqs 14 and 15. The terms with $q_l = q_r = 0$ do not depend on the angle φ_k and refer to the product distribution, which is cylindrically symmetric with respect to the direction of the vector $\mathbf{k}_r$. In particular, if the reagent angular momentum polarization is zero, $K_r = q_r = 0$, then the scattering is always cylindrically symmetric. However, if the reagent angular momentum polarization is nonzero, $K_r \neq 0$, the terms with $q_r \neq 0$ yield product distributions which break the cylindrical symmetry.

The laboratory frame state multipole moments eq 19 are presented in the form

$$\rho_{00}^{(j_C)} = \sqrt{4\pi} N \sum_{K_i,Q_i} \sum_{L,K_r} \frac{\mathbf{c}_{K_i 0}^{0}(K_r,L)}{\sqrt{2K_i + 1}} Y_{K_i Q_i}^{*}(\theta,\phi)\, \mathscr{R}_{K_i Q_i}^{K_r L}(\vartheta,\varphi) \qquad (33)$$

As shown in eq 33, the product angle distribution is expressed as a sum of scalar products of the spherical tensors $Y_{K_i Q_i}(\theta,\phi)$ and $\mathscr{R}_{K_i Q_i}^{K_r L}(\vartheta,\varphi)$.

3. Net Angular Momentum Polarization of the Reaction Products. In this case, the product polarization rank K is assumed to be nonzero and integration over the recoil angles θ and ϕ in eq 19 should be performed. This type of polarization effect was first reported in an atom−molecule reaction by Rettner and Zare.[5] The laboratory-frame product distribution in eq 19 is in general dependent on three vectors $\mathbf{k}_r$, $\mathbf{j}_r$, and $\mathbf{j}_C$. Equation 19 then gives rise to

$$\langle \rho_{KQ}^{(j_C)} \rangle = \frac{4\pi}{2K+1} N \sum_{q_k} \sum_{L,K_r} \mathbf{c}^{K}_{K_i q_k}(K_r,L)\, \mathscr{R}^{K_r L}_{K_i Q_i}(\vartheta,\varphi) \tag{34}$$

4. Angular Distribution of the Product Angular Momenta Polarization. In this case, neither the ranks L nor K_r nor K_i can be set equal to zero. The product-frame product distribution in eq 14 depends on three vectors $\mathbf{k}_r$, $\mathbf{j}_r$, and $\mathbf{j}_C$ and the laboratory-frame product distribution in eq 19 depends on the four vectors $\mathbf{k}_r$, $\mathbf{j}_r$, $\mathbf{k}$, and $\mathbf{j}_C$. Such four-vector correlations have been intensively studied in recent decades in atom−atom and atom−molecule inelastic and reactive scattering.[20,23,24,29,36] The total number of the anisotropy coefficients $\mathbf{c}^{K}_{K_i q_k}(K_r,L)$ in eqs 14 and 19 is in general infinite; however, it can be reduced to a finite number depending on the conditions of experiment as discussed above.

IV. Conclusion

We have used quantum mechanics to derive a compact and completely general theoretical description of the product angular momentum polarization in a general bimolecular reactive scattering experiments. The theory allows for both reactants and both products to possess internal angular momentum, which may be electronic in origin or may arise from the rotation of the reactant or product molecules. The theory as presented in eqs 14 and 19 introduces a new anisotropy transforming parameter $\mathbf{c}^{K}_{K_i q_k}(K_r,L)$ which is independent of all angles and relates the angular momentum polarization of the reactants to that of the product molecule that is measured. The theory presented in the paper assumes that the angular momentum polarization of only one of the reaction products is measured. Further development of the theory could take account of the more general situation where the angular momentum polarization of both scattering products are measured in coincidence.

The derivation of the theory has exposed a new conservation rule. This is embodied in eq 14, which shows that the projection quantum number q_k arising from the coupling of reactant angular momenta, is conserved in the product angular momentum state multipole $\rho^{(j_C)}_{K q_k}$. This new conservation rule comes about through the fact that all angular momenta are projected onto the product recoil momentum vector.

Expressions are presented (eqs 14 and 19) for the product angular momentum state multipoles (i.e., their angular momentum polarization) in both a helicity representation, where the product angular momentum is projected onto the product relative recoil vector $\mathbf{k}$ and in a laboratory frame representation.

The laboratory frame product angular momentum distribution as expressed in eq 19, or in the form in eq 22, provides a powerful tool for experimentalist because it permits the determination from experiment of a set of the angle independent anisotropy-transforming coefficients $\mathbf{c}^{K}_{K_i q_k}(K_r,L)$ for any inelastic or reactive collision process irrespectively to the reaction mechanism.

As shown above, the coefficients $\mathbf{c}^{K}_{K_i q_k}(K_r,L)$ are also directly related to the solution of the quantum scattering theory equations and in principle can be computed from the ab initio theory. Simultaneous determination of the anisotropy coefficients from experiment and comparison with their theoretical values will result in realization of the *complete experiment*[1] in the field of the reaction dynamics. The anisotropy coefficients may alternatively be referred to as anisotropy-transforming coefficients as their role is to map the angular momentum anisotropy present in the reactants onto that which is observed through an examination of the reaction products.

Several examples of the use of the formulas to analyze different experimental situations are discussed. A more detailed derivation of most of the underlying theory is presented in notes available in the Supporting Information.

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Appendix A: Scattering Amplitude Expansion

The derivations outlined in this appendix are available in an extended form in the Supporting Information. The scattering wave function $\Psi_{n_r}(E,\mathbf{k}_r,\mathbf{k})$ in eq 2 depends on two vectors $\mathbf{k}_r$ and $\mathbf{k}$ and can be expanded for all distances R over the set of internal fragment wavefunctions and spherical top eigenfunctions or Wigner $\mathbf{D}$ matrices. To find an appropriate form of this expansion, possessing the desired asymptotic boundary conditions, we first consider the expansion of a plane wave moving in the direction $\mathbf{k}_r$:[46,47]

$$e^{i\mathbf{k}_r\mathbf{R}}|v_r j_r m_r\rangle = 4\pi \sum_{l=0}^{\infty} \sum_{m_l=-l}^{l} i^l j_l(k_r R)\, Y^{*}_{lm_l}(\mathbf{k}_r)\, Y_{lm_l}(\mathbf{k})|v_r j_r m_r\rangle \tag{A1}$$

where $j_l(k_rR)$ is a spherical Bessel function and the reagent internal wave function $|v_r j_r m_r\rangle$ is written in the laboratory reference frame.

Projecting the electronic wave function $|v_r j_r m_r\rangle$ in eq A1 onto the direction $\mathbf{k}$ and substituting the unitary relationship for the Wigner rotation matrices,[42]

$$\sum_{m',\Omega_r} \mathbf{D}^{j}_{m\Omega_r}(\varphi,\vartheta,\gamma)\, \mathbf{D}^{j*}_{m'\Omega_r}(\varphi,\vartheta,\gamma) = 1 \tag{A2}$$

applying the Clebsch−Gordan series,[42] and proceeding with a summation over the indices m_l and m', one can transform the expansion in eq A1 into the total angular momentum JM representation. Then, using the asymptotic expression for the spherical Bessel function $j_l(k_rR)$ and proceeding with a summation over l, one can rewrite the plain-wave expansion in eq A1 in the reactant reference frame as (see Supporting Information)

$$\begin{aligned} e^{i\mathbf{k}_r\cdot\mathbf{R}}|v_r j_r \Omega_r\rangle = -\frac{i}{2k_r R} \sum_{J,M,\Omega} (2J+1)[\delta_{\Omega_r,\Omega} e^{ik_r R} - \\ (-1)^{J-j_r}\delta_{\Omega_r,-\Omega} e^{-ik_r R}] \times \\ \mathbf{D}^{J}_{M\Omega_r}(\varphi,\vartheta,\gamma)\, \mathbf{D}^{J*}_{M\Omega}(\phi,\theta,\xi)|v_r j_r \Omega\rangle \end{aligned} \tag{A3}$$

The expansion in eq A3 shows that the asymptotic expression for the total scattering wave function in eq 2 can in general be written in the form

$$\Psi_{n_\mathrm{r}}(E,\mathbf{k}_\mathrm{r},\mathbf{k}) \overset{R\to\infty}{\sim} \mathrm{e}^{\mathrm{i}\mathbf{k}_\mathrm{r}\cdot\mathbf{R}}|\upsilon_\mathrm{r}j_\mathrm{r}\Omega_\mathrm{r}\rangle + \sum_{J,M,\Omega}\sum_{\upsilon j}\frac{\mathrm{i}(2J+1)}{2\sqrt{k^{\mathrm{AB}}_{\upsilon_\mathrm{r}j_\mathrm{r}}k^{\mathrm{CD}}_{\upsilon j}}}\mathbf{T}^{J}_{\upsilon j\Omega;\upsilon_\mathrm{r}j_\mathrm{r}\Omega_\mathrm{r}}\frac{\mathrm{e}^{\mathrm{i}k^{\mathrm{CD}}_{\upsilon j}R}}{R}\mathbf{D}^{J}_{M\Omega_\mathrm{r}}(\varphi,\vartheta,\gamma)\,\mathbf{D}^{J*}_{M\Omega}(\phi,\theta,\xi)|\upsilon j\Omega\rangle \tag{A4}$$

where the **T** matrix is related to the standard **S** matrix by[47]

$$\mathbf{T}^{J}_{\upsilon j\Omega;\upsilon_\mathrm{r}j_\mathrm{r}\Omega_\mathrm{r}} = \delta_{\Omega,\Omega_\mathrm{r}}\delta_{j,j_\mathrm{r}}\delta_{\upsilon,\upsilon_\mathrm{r}} - \mathbf{S}^{J}_{\upsilon j\Omega;\upsilon_\mathrm{r}j_\mathrm{r}\Omega_\mathrm{r}} \tag{A5}$$

The **S** matrix is obtained from the analysis of the asymptotic form of the solution of the coupled differential equations arising in the scattering problem.[46,47,55] The expansion (A4) agrees with the results reported by Pack[49] and by Nikitin and Umanskii;[47] however, it is generalized to the case of an arbitrary inelastic or reactive collision.

Comparison of eqs 2 and A4 gives eq 3.

Appendix B: Derivation of Eq 14

The derivations outlined in this appendix are available in an extended form in the Supporting Information. Substituting eq 3 into eq 5, using the Clebsch−Gordan series, and performing a summation over the indices M and M', on can rewrite eq 5 in the form

$$\sigma_{j'\Omega',\,j\Omega;\,j_\mathrm{r}\Omega'_\mathrm{r},\,j_r\Omega_\mathrm{r}}(\mathbf{k}_\mathrm{r},\mathbf{k}) = \frac{1}{4(k^{\mathrm{AB}}_{\upsilon_\mathrm{r}j_\mathrm{r}})^2}\sum_{J}\sum_{J'}(2J+1)(2J'+1)(-1)^{\Omega_\mathrm{r}-\Omega} \times \sum_{K_i\alpha\alpha'}\sum_{\beta'}C^{K_i\alpha'}_{J-\Omega_\mathrm{r}J'\Omega'_\mathrm{r}}C^{K_i\beta'}_{J-\Omega J'\Omega'}\mathbf{D}^{K_i}_{\alpha\alpha'}(\varphi,\vartheta,\gamma) \times \mathbf{D}^{K_i*}_{\alpha\beta'}(\phi,\theta,\xi)\mathbf{T}^{\mathrm{CD},J*}_{\upsilon j\Omega,\upsilon_\mathrm{r}j_\mathrm{r}\Omega_\mathrm{r}}\mathbf{T}^{\mathrm{CD},J'}_{\mathrm{v}'j'\Omega',\upsilon'_\mathrm{r}j_\mathrm{r}\Omega'_\mathrm{r}} \tag{B1}$$

Partially transforming this generalized cross section so that the reactant angular momenta are projected onto the laboratory z-axis, multiplying by the reagent density matrix, averaging over m_r and m'_r as indicated in eq 6, and then transforming the state multipoles (eq 7) to the product recoil axis system (see eq 13), one can rewrite the expression for the generalized cross section as

$$\sigma_{j'\Omega',j\Omega}(\mathbf{k}_\mathrm{r},\mathbf{k}) = \sum_{K_\mathrm{r},Q_\mathrm{r}}(-1)^{K_\mathrm{r}-Q_\mathrm{r}-j_\mathrm{r}-\Omega}\sum_{q_\mathrm{r}}\rho^{(j_\mathrm{r})}_{K_\mathrm{r}q_\mathrm{r}}\mathbf{D}^{K_\mathrm{r}*}_{Q_\mathrm{r}q_\mathrm{r}}(\phi,\theta,\xi) \times \frac{1}{4(k^{\mathrm{AB}}_{\upsilon_\mathrm{r}j_\mathrm{r}})^2}\sum_{\Omega_\mathrm{r}\Omega'_\mathrm{r}}\sum_{J}\sum_{J'}(2J+1)(2J'+1) \times \sum_{K_i\alpha\alpha'}\sum_{\beta'}\mathbf{D}^{K_i}_{\alpha\alpha'}(\varphi,\vartheta,\gamma)C^{K_i\alpha'}_{J-\Omega_\mathrm{r}J'\Omega'_\mathrm{r}} \times \mathbf{D}^{K_i*}_{\alpha\beta'}(\phi,\theta,\xi)C^{K_i\beta'}_{J-\Omega J'\Omega'}\mathbf{D}^{K_\mathrm{r}*}_{-Q_\mathrm{r}\alpha'}(\varphi,\vartheta,\gamma)C^{K_\mathrm{r}\alpha'}_{j_\mathrm{r}-\Omega_\mathrm{r}j_\mathrm{r}\Omega'_\mathrm{r}}\left\{\mathbf{T}^{\mathrm{CD},J*}_{\upsilon j\Omega,\upsilon_\mathrm{r}j_\mathrm{r}\Omega_\mathrm{r}}\mathbf{T}^{CD,J'}_{\upsilon'j'\Omega',\upsilon'_\mathrm{r}j_\mathrm{r}\Omega'_\mathrm{r}}\right\} \tag{B2}$$

where q_r is the projection of the reagent multipole rank K_r onto the product recoil axis **k**.

The total integral cross section, σ_0, which enters eq 9 is given by $\sigma_0 = (2j_\mathrm{C}+1)^{-1/2}\langle\mathrm{Tr}[\,\sigma^{(j_\mathrm{c})}_{\Omega'_\mathrm{c},\Omega_\mathrm{c}}(\mathbf{k}_\mathrm{r},\mathbf{k})]\rangle$ for the case when there is no reactant polarization and can be shown to be given by (see Supporting Information)

$$\sigma_0 = \frac{\pi}{(k^{\mathrm{AB}}_{\upsilon_\mathrm{r}j_\mathrm{r}})^2}\sum_{J}\frac{(2J+1)}{(2j_\mathrm{r}+1)}\sum_{j_\mathrm{D}}\sum_{\Omega,\Omega_\mathrm{r}}\{j_\mathrm{C}j_\mathrm{D}j\}\left|\mathbf{T}^{\mathrm{CD},J}_{\upsilon j\Omega,\upsilon_\mathrm{r}j_\mathrm{r}\Omega_\mathrm{r}}\right|^2 \tag{B3}$$

where the symbol $\{j_\mathrm{C}j_\mathrm{D}j\}$ means that the corresponding three quantum numbers obey the triangle rule: $|j_\mathrm{C} - j_\mathrm{D}| \le j \le j_\mathrm{C} + j_\mathrm{D}$.

Equation B2 is now substituted into eq 8, and the result is used in eq 9. The summations over the indices Ω_C, Ω'_C, and Ω_D are then performed using eq 8.7.3.(12) of ref 42 and transforming from the spherical angles ϕ, θ, ξ and φ, ϑ, γ to the spherical angles φ_k, ϑ_k in Figure 1 using the addition theorem for the Wigner **D** matrices,[41,42] the C fragment product state multipole can be expressed in the form (see Supporting Information)

$$\rho^{j_\mathrm{C}}_{Kq_k}(\mathbf{k}_\mathrm{r},\mathbf{k}) = \left\{\frac{\sqrt{\pi}}{2k^{\mathrm{AB}}_{\upsilon'_\mathrm{r}j_\mathrm{r}}k^{\mathrm{AB}}_{\upsilon_\mathrm{r}j_\mathrm{r}}}\frac{\delta_{q_i,q_k}}{\sigma_0}\right\}\sum_{K_i,\alpha'}\sum_{L,K_\mathrm{r}}\sum_{\nu_\mathrm{D},j_\mathrm{D}}\sum_{j,\Omega}\sum_{j',\Omega'}\sum_{\Omega_\mathrm{r}\Omega'_\mathrm{r}}\sum_{J,J'} \times \frac{(2J+1)\sqrt{(2K+1)(2j+1)(2K_\mathrm{r}+1)(2L+1)}}{\sqrt{(2j_\mathrm{r}+1)}} \times (-1)^{j_\mathrm{C}+j_\mathrm{D}}(-1)^{j+K}\,C^{K_\mathrm{r}\alpha'}_{K_\mathrm{r}\alpha'L0}C^{j_\mathrm{r}\Omega'_\mathrm{r}}_{J_\mathrm{r}\Omega_rK_\mathrm{r}\alpha'}C^{j'\Omega'}_{j\Omega\;K-q_k}C^{j'\Omega'_\mathrm{r}}_{J\Omega_rK_i\alpha'} \times C^{J'\Omega'}_{J\Omega\;K_i-q_k}\begin{Bmatrix} j_\mathrm{C} & j_\mathrm{D} & j \\ j' & K & j_\mathrm{C} \end{Bmatrix}\left\{\left(\mathbf{T}^{\mathrm{CD},J}_{\nu j\Omega,\nu_\mathrm{r}j_\mathrm{r}\Omega_\mathrm{r}}\right)\mathbf{T}^{\mathrm{CD},J'}_{\nu'j'\Omega',\nu'_\mathrm{r}j_\mathrm{r}\Omega'_\mathrm{r}}\right\} \times \left\{\sum_{q_\mathrm{r},q_l}C^{K_iq_i}_{Lq_lK_\mathrm{r}q_\mathrm{r}}Y_{Lq_i}(\vartheta_k,\varphi_k)\rho^{(j_\mathrm{r})}_{K_\mathrm{r}q_\mathrm{r}}\right\} \tag{B4}$$

This product state multipole can be rewritten as

$$\rho^{(j_\mathrm{C})}_{Kq_k}(\mathbf{k}_\mathrm{r},\mathbf{k}) = N\sum_{K_i}\sum_{L,K_\mathrm{r}}\mathbf{c}^{K}_{K_iq_k}(K_\mathrm{r},L)\;\mathscr{R}^{K_\mathrm{r}L}_{K_iq_k}(\vartheta_k,\varphi_k) \tag{B5}$$

where

$$\mathbf{c}^{K}_{K_iq_k}(K_\mathrm{r},L) = N^{-1}\left\{\frac{\sqrt{\pi}}{\sigma_0 2k^{\mathrm{AB}}_{\upsilon'_\mathrm{r}j\mathrm{r}}k^{\mathrm{AB}}_{\upsilon_\mathrm{r}j\mathrm{r}}}\right\}\sum_{\nu_\mathrm{D},j_\mathrm{D}}\sum_{j,\Omega}\sum_{j',\Omega'}\sum_{J}\sum_{J'}\sum_{\alpha'} \times \frac{(2J+1)\sqrt{(2K+1)(2j+1)(2K_\mathrm{r}+1)(2L+1)}}{\sqrt{(2j_\mathrm{r}+1)}} \times (-1)^{j_\mathrm{C}+j_\mathrm{D}}(-1)^{j+K}C^{K_\mathrm{i}\alpha'}_{K_\mathrm{r}\alpha'L0}C^{j_\mathrm{r}\Omega'_\mathrm{r}}_{j_\mathrm{r}\Omega_\mathrm{r}K_\mathrm{r}\alpha'}C^{j'\Omega'}_{j\Omega K-q_k} \times C^{J'\Omega'_\mathrm{r}}_{J\Omega_\mathrm{r}K_i\alpha'}C^{J'\Omega'}_{J\Omega K_i-q_k}\begin{Bmatrix} j_\mathrm{C} & j_\mathrm{D} & j \\ j' & K & j_\mathrm{C} \end{Bmatrix}\left\{\left(\mathbf{T}^{\mathrm{CD},J}_{\nu j\Omega,\nu_\mathrm{r}j_\mathrm{r}\Omega_\mathrm{r}}\right)^{*}\mathbf{T}^{\mathrm{CD},J'}_{\nu'j'\Omega',\nu'_rj_\mathrm{r}\Omega'_\mathrm{r}}\right\} \tag{B6}$$

and

$$\mathscr{R}^{K_\mathrm{r}L}_{K_iq_k}(\vartheta_k,\varphi_k) = \sum_{q_\mathrm{r}}\sum_{\lambda} C^{K_iq_k}_{L\lambda K_\mathrm{r}q_\mathrm{r}} Y_{L\lambda}(\vartheta_k,\varphi_k)\rho^{(j_r)}_{K_\mathrm{r}q_\mathrm{r}} \qquad \text{(B7)}$$

The “normalization” constant N appearing in eqs B5 and B6 is defined in the main section of the text.

Supporting Information Available: Notes containing a detailed derivation of most of the formulas in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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