

**On the quantum and quasiclassical angular distributions of photofragments**J. Alberto Beswick<sup>1,a)</sup> and Richard N. Zare<sup>2</sup><sup>1</sup>Laboratoire Collisions, Agrégats, Réactivité, UMR 5589 du CNRS IRSAMC, Université Paul Sabatier, 31062 Toulouse, France<sup>2</sup>Department of Chemistry, Stanford University, Stanford, California 94305-5080, USA

(Received 14 August 2008; accepted 25 September 2008; published online 28 October 2008)

Quantum and quasiclassical expressions for the angular distribution of photofragments from an initially polarized precursor molecule are compared under the conditions of a one-photon electric dipole transition to a repulsive state followed by prompt axial recoil into two separating fragments. The treatment is most readily applicable to diatomic molecules, but it is more general than that. It is shown that when the rotational and electronic angular momentum  $J_i$  and its projection along the body-fixed  $z$  axis  $\Omega_i$  are well defined in the initial state, the quantum and quasiclassical expressions are identical for any initial polarization of the molecule prior to photolysis and for all values of  $J_i$  and  $\Omega_i$ . For the particular case of an  $|J_i\Omega_iM_i\rangle$  selected state this is in agreement with a previous result [T. Seideman, Chem. Phys. Lett. **253**, 279 (1996)]. Moreover, the quasiclassical expression is still a good approximation even when the initial state is a coherent superposition of  $|J_i, \Omega_i, M_i\rangle$  levels for the same  $\Omega_i$ . This near identity still pertains even when  $\Omega_i$  is not well defined for a parallel transition ( $\Delta\Omega=0$ ) but fails for a perpendicular transition ( $\Delta\Omega=\pm 1$ ) if the initial state is in a coherent superposition of  $\Omega_i$  states differing by  $\pm 2$ . These conclusions apply to preparation schemes employing optical excitation, static inhomogeneous and/or homogeneous electric and/or magnetic fields, as well as to molecules physisorbed on solids or clusters. We discuss the importance of these results in the interpretation of photofragment distributions when some other angular momenta are involved, such as electronic angular momentum, with and without nuclear spin, coupled to molecular rotation, asymmetric top rotational angular momentum, or internal vibrational angular momentum in polyatomics. © 2008 American Institute of Physics.

[DOI: 10.1063/1.3000581]

**I. INTRODUCTION**

Unimolecular photodissociation produces in general anisotropic distributions of the products fragments' relative velocity  $\mathbf{v}$  and their angular momenta  $\mathbf{j}$ .<sup>1-3</sup> These vector properties have received considerable experimental and theoretical attention lately<sup>4-6</sup> as a means to obtain crucial information on structure, symmetry, and energetics of dissociation dynamics as well as a way to produce polarized fragments for use in applications such as spin-dependent effects in atomic, molecular, and surface physics.

The quantum mechanical treatment of the angular distribution of photofragments under the conditions of a one-photon electric dipole transition in a diatomic molecule was derived by Zare.<sup>7,8</sup> For an initially isolated randomly oriented precursor molecule photodissociated by linearly polarized light, the laboratory angularly resolved photofragment intensity has the now familiar expression

$$I(\theta) \propto 1 + \beta P_2(\cos \theta), \quad (1)$$

with the laboratory  $Z$  axis chosen to be in the direction of the electric vector of the light beam. The anisotropy parameter  $\beta$  in Eq. (1) involves the sum products of radial matrix elements and  $3-j$  symbols depending on the initial  $J_i$  and final  $J=J_i$ ,  $J_i \pm 1$  total rotational quantum numbers, as well as on

the initial  $\Omega_i$  and final  $\Omega$  quantum numbers associated with projection of  $\mathbf{J}$  on the internuclear axis. For prompt dissociation, for which the axial recoil approximation is valid,  $\beta$  takes the limiting values  $+2$  and  $-1$  for pure parallel ( $\Delta\Omega=0$ ) and pure perpendicular ( $\Delta\Omega=\pm 1$ ) transitions. These limiting values can be interpreted classically since they correspond, respectively, to a  $\cos^2 \theta$  and a  $\sin^2 \theta$  absorption probability, i.e., proportional to  $|\boldsymbol{\mu} \cdot \boldsymbol{\epsilon}_i|^2$ , where  $\boldsymbol{\mu}$  is the electric dipole transition moment and  $\boldsymbol{\epsilon}_i$  is the light polarization vector.

In addition to the case of initially randomly oriented targets, the angular distribution of the photofragments from an initially selected  $J_i, \Omega_i, M_i$  state was also considered.<sup>8-12</sup> It was shown that the angular distributions are highly oscillatory involving Legendre polynomials up to  $2J_i+2$ .

More recently, Underwood and Powis<sup>13</sup> in their study of photodissociation of polarized diatomic molecules and Dagdikian<sup>14</sup> in the case of vibrationally mediated photodissociation considered the generalization of the above to an oriented or aligned initial state. The calculations involved lengthy angular momentum algebra. Even in the axial recoil limit, the final expressions involve the product of six  $3-j$  symbols. On the other hand, the photofragment angular distribution following photolysis of an ensemble of symmetric-top molecules in a single  $|J_i K_i M_i\rangle$  state ( $K_i$  replacing the  $\Omega_i$  in this case) has been analyzed by Choi and Bernstein<sup>15</sup> using a simple quasiclassical equation of the form

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$$I(\theta) \propto P_{J_i K_i M_i}(\theta) [1 + \beta P_2(\cos \theta)], \quad (2)$$

where  $P_{J_i K_i M_i}(\theta)$  is the (quantum) initial probability to find the prepared molecule with its axis pointing between  $\theta$  and  $\theta+d\theta$ . This very simple equation based on intuitive assumptions concerning the initial angular distribution and prompt dissociation was discussed more rigorously by Zare<sup>16</sup> and by Taatjes *et al.*<sup>17</sup> who suggested modifications to take into account the orientation of the transition dipole moment in the molecular frame and the finite dissociation time. The general validity of Eq. (2) has been questioned because at first sight it appears to be very different from the quantum expression. However, comparison of Eq. (2) with experiment showed good agreement in most cases.<sup>18,19</sup> Seideman<sup>20</sup> compared the quantum and the quasiclassical expressions for the  $M_i$  selected case and concluded that both are identical if it is assumed that the scattering wave functions are independent of the rotational branch (axial recoil limit) and that the transition dipole vector is very simple (a pure parallel or a pure perpendicular transition).

The study of angular distributions for a general initial state concerns molecules which have been prepared by optical excitation, static inhomogeneous and/or homogeneous electric and/or magnetic fields, as well as molecules physisorbed on solids or clusters. The comparison between the quantum and the quasiclassical approaches can therefore be of importance to (1) the assessment of the validity of the quasiclassical equation (2) which being a very simple expression can be very useful to design and interpret experiments and (2) the determination of in which cases quantum interference effects must be taken into account. Thus, this formulation provides additional information on the properties of the initially prepared state.

In this paper we present new theoretical evidence showing that the quasiclassical formula [Eq. (2)] has a wider range of applicability than previously thought. The quasiclassical and quantum expressions are identical for an initial  $J_i, \Omega_i$  state for all possible distributions of  $M_i$ , i.e., whatever is its polarization. In addition, the quasiclassical expression is still a good approximation even when the initial state is a coherent superposition of  $|J_i, \Omega_i, M_i\rangle$  levels for the same  $\Omega_i$ . This near identity still pertains even when  $\Omega_i$  is not well defined for a parallel transition ( $\Delta\Omega=0$ ) but fails for a perpendicular transition ( $\Delta\Omega=\pm 1$ ) if the initial state is in a coherent superposition of  $\Omega_i$  states differing by  $\pm 2$ , in which case quantum interference effects are present.

The organization of this paper is the following. In Sec. II we present the exact quantum and the axial recoil limit expressions for the photofragment angular distribution of a system in a completely general initially prepared state described by its multipole moments and dissociated via a one-photon electric dipole transition. In Sec. III the corresponding quasiclassical equation (2) for the same general initial state is rewritten in terms of a sum of spherical harmonics. This formulation allows a direct comparison with the quantum results; this comparison is presented in Sec. IV. In these sections the initial state is just described as a general linear combination of  $(J_i, \Omega_i, M_i)$ , where  $J_i$  is the molecular rotational angular momentum interacting directly with the pho-

ton field. In Sec. V we discuss how to include other angular momenta that may couple strongly or weakly to the rotational angular momentum, in particular, nuclear spin. We also discuss the common situation where the system is prepared in a coherent superposition of eigenstates and there is a time delay  $\Delta t$  between the preparation step and the photolysis laser pulse. In this case oscillations as a function of  $\Delta t$  are expected.

## II. QUANTUM TREATMENT

The angular distribution of fragments from an initial  $|\varphi_i\rangle$  state excited by a transition operator  $T$  to a final repulsive state at total energy  $E$  is given by

$$I_{\text{quant}}(\theta, \phi) \propto \sum_{J, J'} \sum_{M, M'} (2J+1)^{1/2} (2J'+1)^{1/2} \times \sum_{\Omega} D_{M\Omega}^{J*}(\phi, \theta, 0) \langle \varphi_{\Omega}^{JME} | T | \varphi_i \rangle \times \langle \varphi_i | T | \varphi_{\Omega}^{J'M'E} \rangle D_{M'\Omega}^{J'}(\phi, \theta, 0), \quad (3)$$

where the  $D_{M\Omega}^{J*}(\phi, \theta, 0)$  are Wigner rotational functions with the phase conventions of Ref. 21 and the  $|\varphi_{\Omega}^{JME}\rangle$  are final state continuum states labeled by the good quantum numbers  $J, M$  corresponding to the (rotational and electronic) angular momentum  $\mathbf{J}$  and its projection along the laboratory  $Z$  axis and by  $\Omega$  the quantum number associated with the projection of  $\mathbf{J}$  along the body-fixed  $z$  axis. The body-fixed frame is obtained from the space-fixed frame through positive rotations with Euler angles  $(\phi, \theta, 0)$  so that  $\mathbf{R}$ , the vector connecting the centers of mass of the two fragments, lies on the body-fixed  $z$  axis. It should be noted that  $J_z = (\mathbf{J} \cdot \mathbf{R})/R$  commutes with the Hamiltonian only in the limit  $R \rightarrow \infty$ . Although  $\Omega$  is not a good quantum number, it is always possible, however, to define continuum states labeled by the  $\Omega$  value to which they correlate adiabatically for  $R \rightarrow \infty$ . Thus, in general we have

$$|\varphi_{\Omega}^{JME}\rangle \propto \sum_{\tilde{\Omega}} (2J+1)^{1/2} D_{M\tilde{\Omega}}^{J*}(\phi, \theta, 0) |\psi_{\Omega, \tilde{\Omega}}^{JE}\rangle, \quad (4)$$

where the  $|\psi_{\Omega, \tilde{\Omega}}^{JE}\rangle$  behave asymptotically as<sup>12</sup>

$$|\psi_{\Omega, \tilde{\Omega}}^{JE}\rangle \underset{R \rightarrow \infty}{\propto} \delta_{\Omega, \tilde{\Omega}} \frac{e^{ikR}}{R} |\Omega\rangle + S_{\Omega, \tilde{\Omega}}^{J*}(E) \frac{e^{-ikR}}{R} |\tilde{\Omega}\rangle, \quad (5)$$

with

$$k = \sqrt{2m(E - V(\infty))}/\hbar, \quad (6)$$

where  $m = m_A m_B / (m_A + m_B)$  is the reduced mass for the relative motion of the products  $A$  and  $B$ , and  $V(\infty)$  is the fragmentation limit. In Eq. (4),  $|\Omega\rangle$  are orthogonal states depending on all internal coordinates (electronic and nuclear) of the fragments. Finally,  $S_{\Omega, \tilde{\Omega}}^{J*}(E)$  is the scattering matrix corresponding to the full collision between  $A$  and  $B$ . The particular form chosen in Eq. (5) corresponds to outgoing spherical wave boundary conditions often denoted by a  $(-)$  superscript.

Using the Clebsch–Gordan series,<sup>21</sup> Eq. (3) can be recast in the form

$$\begin{aligned}
I_{\text{quant}}(\theta, \phi) &\propto \sum_{L, \lambda} (2L+1)^{1/2} Y_{L\lambda}(\theta, \phi) \\
&\times \sum_{J, J'} \sum_{M, M'} \sum_{\Omega} (-)^{\Omega-M} (2J+1)^{1/2} (2J'+1)^{1/2} \\
&\times \begin{pmatrix} J & J' & L \\ M & -M' & -\lambda \end{pmatrix} \begin{pmatrix} J & J' & L \\ \Omega & -\Omega & 0 \end{pmatrix} \\
&\times \langle \varphi_{\Omega}^{JME} | T | \varphi_i \rangle \langle \varphi_i | T | \varphi_{\Omega}^{J'M'} \rangle. \quad (7)
\end{aligned}$$

Equation (7) provides the most general angular distribution of fragmentation into two fragments. The operator  $T$  can represent a one-photon or a multiphoton transition operator for the case of direct photodissociation or an intramolecular coupling  $T=H-H_0$  for the case of predissociation, in which case  $\varphi_i$  is an excited bound state of  $H_0$ .

### A. One-photon electric dipole transitions

For one-photon electric-dipole-allowed transition we shall have  $T \propto \boldsymbol{\mu} \cdot \boldsymbol{\epsilon}_i$ , where  $\boldsymbol{\epsilon}_i$  is the photon polarization vec-

tor and  $\boldsymbol{\mu}$  is the electric dipole moment operator. A general initial state of the system prior to photolysis can be written as

$$|\varphi_i\rangle \propto \sum_{J_i, \Omega_i, M_i} a_{J_i, \Omega_i, M_i} (2J_i+1)^{1/2} D_{M_i, \Omega_i}^{J_i*}(\phi, \theta, \gamma) |\psi_{\Omega_i}^{J_i}\rangle, \quad (8)$$

where  $|\psi_{\Omega_i}^{J_i}\rangle$  are orthogonal vibronic kets depending on all electronic and vibrational coordinates. It should be noted at this point that the body-fixed axis of quantization corresponds to the vector distance  $\mathbf{R}$  between the center of mass of the two moieties giving rise to the products. Only for a diatomic and some other particular cases, it will coincide with a bond axis or a symmetry axis of the molecule. For the  $ABC+h\nu \rightarrow A+BC$  case, for instance,  $\mathbf{R}$  will be the vector from  $A$  to the center of mass of  $BC$  which in the nonlinear configuration and finite  $R$  will not coincide in general with the principal axis of inertia. Therefore, an initial nonlinear bound state of  $ABC$  will be a linear combination of  $\Omega_i$  states.

Using

$$\begin{aligned}
\langle \varphi_{\Omega}^{JME} | \boldsymbol{\mu} \cdot \boldsymbol{\epsilon}_i | \varphi_i \rangle &= (2J+1)^{1/2} \sum_{J_i, \Omega_i, M_i} a_{J_i, \Omega_i, M_i} (2J_i+1)^{1/2} \sum_{\eta} (-)^{\eta} (\boldsymbol{\epsilon}_i)_{-\eta} \begin{pmatrix} J_i & 1 & J \\ M_i & -\eta & M \end{pmatrix} \\
&\times \sum_{\Omega_i, q, \tilde{\Omega}} (-)^{M-\tilde{\Omega}} \begin{pmatrix} J_i & 1 & J \\ -\Omega_i & -q & \tilde{\Omega} \end{pmatrix} \langle \psi_{\Omega, \tilde{\Omega}}^{JE} | (\boldsymbol{\mu})_q | \psi_{\Omega_i}^{J_i} \rangle, \quad (9)
\end{aligned}$$

one gets

$$\begin{aligned}
I_{\text{quant}}(\theta, \phi) &\propto \sum_{L, \lambda} (2L+1)^{1/2} Y_{L\lambda}(\theta, \phi) \sum_{J, J'} \sum_{M, M'} \sum_{\Omega} (-)^{\Omega-M} (2J+1)^{1/2} (2J'+1)^{1/2} \begin{pmatrix} J & J' & L \\ M & -M' & -\lambda \end{pmatrix} \begin{pmatrix} J & J' & L \\ \Omega & -\Omega & 0 \end{pmatrix} \\
&\times \sum_{J_i, \Omega_i, M_i} (2J_i+1)^{1/2} \sum_{\eta} (-)^{\eta} (\boldsymbol{\epsilon}_i)_{-\eta} \begin{pmatrix} J_i & 1 & J \\ -M_i & -\eta & M \end{pmatrix} \sum_{\Omega_i, q, \tilde{\Omega}} (-)^{M-\tilde{\Omega}} \begin{pmatrix} J_i & 1 & J \\ -\Omega_i & -q & \tilde{\Omega} \end{pmatrix} \langle \psi_{\Omega, \tilde{\Omega}}^{JE} | (\boldsymbol{\mu})_q | \psi_{\Omega_i}^{J_i} \rangle \\
&\times \sum_{J'_i, \Omega'_i, M'_i} (2J'_i+1)^{1/2} \sum_{\eta'} (-)^{\eta'} (\boldsymbol{\epsilon}_i)_{-\eta'}^* \begin{pmatrix} J'_i & 1 & J' \\ -M'_i & -\eta' & M' \end{pmatrix} \\
&\times \sum_{\Omega'_i, q', \tilde{\Omega}'} (-)^{M'-\tilde{\Omega}'} \begin{pmatrix} J'_i & 1 & J' \\ -\Omega'_i & -q' & \tilde{\Omega}' \end{pmatrix} \langle \psi_{\Omega, \tilde{\Omega}'}^{J'E} | (\boldsymbol{\mu})_{q'} | \psi_{\Omega'_i}^{J'_i} \rangle^* \langle J'_i \Omega'_i M'_i | \rho | J_i \Omega_i M_i \rangle, \quad (10)
\end{aligned}$$

where

$$\langle J'_i \Omega'_i M'_i | \rho | J_i \Omega_i M_i \rangle = a_{J'_i \Omega'_i M'_i}^* a_{J_i \Omega_i M_i} \quad (11)$$

are the elements of the initial-state density matrix. Introducing the *covariant* multipole moments of the initial state via

$$\rho_{K_i Q_i}(J'_i \Omega'_i M'_i, J_i \Omega_i M_i) = \sum_{M_i, M'_i} (-)^{J'_i - M'_i} (2K_i+1)^{1/2} \begin{pmatrix} J_i & J'_i & K_i \\ M_i & -M'_i & Q_i \end{pmatrix} J'_i \Omega'_i M'_i \rho | J_i \Omega_i M_i \rangle \quad (12)$$

with its inverse

$$\langle J'_i \Omega'_i M'_i | \rho | J_i \Omega_i M_i \rangle = (-)^{J'_i - M'_i} \sum_{K_i, Q_i} (2K_i+1)^{1/2} \begin{pmatrix} J_i & J'_i & K_i \\ M_i & -M'_i & Q_i \end{pmatrix} \rho_{K_i Q_i}(J'_i \Omega'_i, J_i \Omega_i), \quad (13)$$

we can rewrite Eq. (10) as

$$\begin{aligned}
I_{\text{quant}}(\theta, \phi) &\propto \sum_{L, \lambda} (2L+1)^{1/2} Y_{L\lambda}(\theta, \phi) \sum_{K_i, Q_i} \sum_{J_i, \Omega_i, J'_i, \Omega'_i} \rho_{K_i, Q_i}(J'_i \Omega'_i, J_i \Omega_i) (2K_i+1)^{1/2} (2J_i+1)^{1/2} (2J'_i+1)^{1/2} \\
&\times \sum_{\eta} (-)^{\eta} (\boldsymbol{\epsilon}_i)_{-\eta} \sum_{\eta'} (-)^{\eta'} (\boldsymbol{\epsilon}_i)_{-\eta'}^* \sum_{\Omega, q, \tilde{\Omega}, q', \tilde{\Omega}'} \sum_{J, J'} (2J+1)(2J'+1) \\
&\times (-)^{J'_i + \Omega - \tilde{\Omega} - \tilde{\Omega}'} \begin{pmatrix} J & J' & L \\ \Omega & -\Omega & 0 \end{pmatrix} \begin{pmatrix} J_i & 1 & J \\ -\Omega_i & -q & \tilde{\Omega} \end{pmatrix} \begin{pmatrix} J'_i & 1 & J' \\ -\Omega'_i & -q' & \tilde{\Omega}' \end{pmatrix} \langle \psi_{\Omega, \tilde{\Omega}}^{JE} | (\boldsymbol{\mu})_q | \psi_{\Omega_i}^{J_i} \rangle \langle \psi_{\Omega, \tilde{\Omega}'}^{J'E} | \\
&\times (\boldsymbol{\mu})_{q'} | \psi_{\Omega'_i}^{J'_i} \rangle^* S_1(J, J', L, \lambda, J_i, J'_i, K_i, Q_i, \eta, \eta'), \tag{14}
\end{aligned}$$

where

$$\begin{aligned}
S_1(J, J', L, \lambda, J_i, J'_i, K_i, Q_i, \eta, \eta') &= \sum_{M_i, M'_i, M, M'} (-)^{M'-M'_i} \begin{pmatrix} J_i & 1 & J \\ -M_i & -\eta & M \end{pmatrix} \begin{pmatrix} J & J' & L \\ M & -M' & -\lambda \end{pmatrix} \begin{pmatrix} J'_i & 1 & J' \\ -M'_i & -\eta' & M' \end{pmatrix} \\
&\times \begin{pmatrix} J_i & J'_i & K_i \\ M_i & -M'_i & Q_i \end{pmatrix} \tag{15}
\end{aligned}$$

involves the sum over all space-fixed components. Using Eq. (A2) of Appendix A we can write Eq. (14) as

$$\begin{aligned}
I_{\text{quant}}(\theta, \phi) &\propto \sum_{L, \lambda} (2L+1)^{1/2} Y_{L\lambda}(\theta, \phi) \sum_{K_i, Q_i} (-)^{K_i} (2K_i+1)^{1/2} \sum_{J_i, \Omega_i, J'_i, \Omega'_i} (2J_i+1)^{1/2} (2J'_i+1)^{1/2} \rho_{K_i, Q_i}(J'_i \Omega'_i, J_i \Omega_i) \\
&\times \sum_{P, p} (2P+1)^{1/2} E_{Pp} \sum_{\Omega, q, \tilde{\Omega}, q', \tilde{\Omega}'} (-)^{J'_i - J_i + \Omega - \tilde{\Omega} - \tilde{\Omega}' - 1} \begin{pmatrix} P & K_i & L \\ p & Q_i & \lambda \end{pmatrix} \sum_{J, J'} (-)^{J'} (2J+1)(2J'+1) \begin{pmatrix} J & J' & L \\ \Omega & -\Omega & 0 \end{pmatrix} \\
&\times \begin{pmatrix} J_i & 1 & J \\ -\Omega_i & -q & \tilde{\Omega} \end{pmatrix} \begin{pmatrix} J'_i & 1 & J' \\ -\Omega'_i & -q' & \tilde{\Omega}' \end{pmatrix} \begin{pmatrix} 1 & J_i & J \\ P & K_i & L \\ 1 & J'_i & J' \end{pmatrix} \langle \psi_{\Omega, \tilde{\Omega}}^{JE} | (\boldsymbol{\mu})_q | \psi_{\Omega_i}^{J_i} \rangle \langle \psi_{\Omega, \tilde{\Omega}'}^{J'E} | (\boldsymbol{\mu})_{q'} | \psi_{\Omega'_i}^{J'_i} \rangle^*, \tag{16}
\end{aligned}$$

where

$$\begin{aligned}
E_{Pp}(\boldsymbol{\epsilon}_i) &\equiv (2P+1)^{1/2} \sum_{\eta, \eta'} (-)^{\eta} \\
&\times (\boldsymbol{\epsilon}_i)_{-\eta} (\boldsymbol{\epsilon}_i)_{-\eta'}^* \begin{pmatrix} 1 & 1 & P \\ -\eta & \eta' & -p \end{pmatrix} \tag{17}
\end{aligned}$$

is the light polarization tensor.

Equation (16) constitutes the most general rigorous expression for the fragments' angular distribution in a one-photon electric dipole photodissociation process for a general initial state described by its multipole moments  $\rho_{K_i, Q_i}$ , and it is valid for integers as well as for half integer quantum numbers. The covariant multipole moments defined by Eq. (12) are normalized such that  $\rho_{00}(J_i, \Omega_i) = \sum_{M_i} \langle J_i \Omega_i M_i | \rho | J_i \Omega_i M_i \rangle / (2J_i+1)$ .

Because from Eq. (17)  $P$  is restricted to 0, 1, and 2 (one-photon electric dipole transitions) and from Eq. (12)  $K_i$  runs from 0 to  $J_{i \text{ max}}$ , the angular distribution includes spherical harmonics up to  $L_{\text{max}} = 2J_{i \text{ max}} + 2$ . This result is well known,<sup>13</sup> and it also applies to photoionization from oriented molecules.<sup>22</sup> As it has been noted before,<sup>13</sup> if the  $Q_i=0$  are the only nonzero elements of  $\rho_{K_i, Q_i}$  (axially symmetric initial state), then for linear polarization ( $p=0$  if the laboratory  $Z$  axis is chosen along the polarization vector of the photon)

we have  $\lambda=0$  and the angular distribution is also cylindrically symmetric around the laboratory  $Z$  axis. If  $Q_i \neq 0$  elements are nonzero, then even for linear polarization the angular distribution will be noncylindrically symmetric and dependent on  $\phi$ .

## B. Prompt fragmentation: Axial recoil limit

In the *axial recoil* limit where fragmentation is fast compared with the rotational period of the system, the following follows.

- (1) The body-fixed projection  $\Omega$  of the final state is an almost good quantum number [Coriolis (or helicity) decoupling].
- (2) The radial matrix elements of the transition dipole operator  $\langle \psi_{\alpha\Omega}^{J'E} | (\boldsymbol{\mu})_q | \psi_{\alpha\Omega_i}^{J_i} \rangle$  for  $J=J_i$ ,  $J_i \pm 1$  depend very little on  $J$  (branch independent).

Under these conditions, we can replace in Eq. (16)  $\tilde{\Omega} = \tilde{\Omega}' = \Omega$  and  $\langle \psi_{\alpha\Omega}^{J'E} | (\boldsymbol{\mu})_q | \psi_{\alpha\Omega_i}^{J_i} \rangle$  for  $(J=J_i, J_i \pm 1)$  by  $\langle \psi_{\alpha\Omega}^{J'E} | (\boldsymbol{\mu})_q | \psi_{\alpha\Omega_i}^{J_i} \rangle$  with the result (see Appendix B)

$$\begin{aligned}
I_{\text{quant}}(\theta, \phi) \propto & \sum_{L, \lambda} (2L+1)^{1/2} Y_{L\lambda}(\theta, \phi) \sum_{J_i, \Omega_i} \sum_{J'_i, \Omega'_i} (-)^{J'_i - \Omega'_i} (2J_i+1)^{1/2} (2J'_i+1)^{1/2} \sum_{K_i, Q_i} (2K_i+1)^{1/2} \rho_{K_i, Q_i}(J'_i, \Omega'_i, J_i, \Omega_i) \\
& \times \begin{pmatrix} J_i & J'_i & K_i \\ \Omega_i & -\Omega'_i & \Omega'_i - \Omega_i \end{pmatrix} \sum_{P, p} (2P+1)^{1/2} E_{Pp}(\epsilon_i) \begin{pmatrix} P & K_i & L \\ p & Q_i & \lambda \end{pmatrix} \\
& \times \sum_{q, q'} (-)^{q'} \begin{pmatrix} P & K_i & L \\ q - q' & \Omega_i - \Omega'_i & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & P \\ -q & q' & q - q' \end{pmatrix} M_q(J_i, \Omega_i) M_{q'}^*(J'_i, \Omega'_i), \tag{18}
\end{aligned}$$

where we have defined

$$M_q(J_i, \Omega_i) \equiv \langle \psi_{\Omega_i+q, \Omega_i+q}^{J_i E} | \boldsymbol{\mu}_q | \psi_{\Omega_i}^{J_i} \rangle. \tag{19}$$

### 1. Linearly polarized light

For linearly polarized light along the laboratory  $Z$  axis  $p=0$  and only  $P=0$  and  $2$  contributes to Eq. (17). We then have from Eq. (18),

$$\begin{aligned}
I_{\text{quant}}(\theta, \phi) \propto & \sum_{L, \lambda} Y_{L\lambda}(\theta, \phi) \sum_{J_i, \Omega_i} \sum_{J'_i, \Omega'_i} (-)^{J'_i - \Omega'_i} (2J_i+1)^{1/2} (2J'_i+1)^{1/2} \sigma_{\Omega_i}(J_i, J'_i) \sum_{K_i} \rho_{K_i, -\lambda}(J'_i, \Omega'_i, J_i, \Omega_i) \begin{pmatrix} J_i & J'_i & K_i \\ \Omega_i & -\Omega'_i & \Omega'_i - \Omega_i \end{pmatrix} \\
& \times \left[ \delta_{K_i, L} \delta_{\Omega_i, \Omega'_i} (-)^\lambda + \frac{\sqrt{30}}{\sigma_{\Omega_i}(J_i, J'_i)} (2L+1)^{1/2} (2K_i+1)^{1/2} \begin{pmatrix} 2 & K_i & L \\ 0 & -\lambda & \lambda \end{pmatrix} \sum_{q, q'} (-)^{q'} \begin{pmatrix} 2 & K_i & L \\ q' - q & \Omega'_i - \Omega_i & 0 \end{pmatrix} \right. \\
& \left. \times \begin{pmatrix} 1 & 1 & 2 \\ -q & q' & q - q' \end{pmatrix} M_q(J_i, \Omega_i) M_{q'}^*(J'_i, \Omega'_i), \right] \tag{20}
\end{aligned}$$

where we have defined

$$\sigma_{\Omega_i}(J_i, J'_i) = \sum_q M_q(J_i, \Omega_i) M_q^*(J'_i, \Omega_i). \tag{21}$$

This result can be compared to similar expressions found by Underwood and Powis.<sup>13</sup> With an obvious change in notations, Eq. (20) agrees with Eq. (2.30b) of Ref. 13 except for a missing factor  $(2P+1)^{1/2}$  which has been corrected in an erratum.<sup>23</sup>

## III. QUASICLASSICAL TREATMENT

### A. The initial angular probability

With  $\varphi_i$  given by Eq. (8), the probability density of finding the molecule's body-fixed vector  $\mathbf{R}$  pointing into the solid angle element  $d(\cos \theta)d\phi$  along  $(\theta, \phi)$  is given by

$$\begin{aligned}
P_i(\theta, \phi) \propto & \sum_{J_i, J'_i, M_i, M'_i, \Omega_i} \langle J'_i M'_i \Omega_i | \rho | J_i \Omega_i M_i \rangle (2J_i+1)^{1/2} \\
& \times (2J'_i+1)^{1/2} D_{M_i, \Omega_i}^{J_i}(\phi, \theta, \gamma) D_{M'_i, \Omega_i}^{J'_i}(\phi, \theta, \gamma), \tag{22}
\end{aligned}$$

with  $\langle J'_i M'_i \Omega_i | \rho | J_i \Omega_i M_i \rangle$  defined by Eq. (11).

Using the Clebsch–Gordan series,<sup>21</sup> we can write

$$\begin{aligned}
P_i(\theta, \phi) = & \sum_{J_i, J'_i, M_i, M'_i, \Omega_i} \langle J'_i M'_i \Omega_i | \rho | J_i \Omega_i M_i \rangle \\
& \times \left( \frac{2J_i+1}{4\pi} \right)^{1/2} \left( \frac{2J'_i+1}{4\pi} \right)^{1/2} \\
& \times (-)^{M'_i - \Omega_i} \sum_{K_i, Q_i} (2K_i+1) \begin{pmatrix} J_i & J'_i & K_i \\ M_i & -M'_i & Q_i \end{pmatrix} \\
& \times \begin{pmatrix} J_i & J'_i & K_i \\ \Omega_i & -\Omega_i & 0 \end{pmatrix} D_{Q_i, 0}^{K_i}(\phi, \theta, 0), \tag{23}
\end{aligned}$$

and in terms of the initial multipole equation (13), it reads [compare with Eq. (7.6.6) of Ref. 24]

$$\begin{aligned}
P_i(\theta, \phi) = & \sum_{J_i, J'_i, \Omega_i} (-)^{J'_i - \Omega_i} \left( \frac{2J_i+1}{4\pi} \right)^{1/2} \left( \frac{2J'_i+1}{4\pi} \right)^{1/2} \\
& \times \sum_{K_i, Q_i} (2K_i+1)^{1/2} \rho_{K_i, Q_i}(J'_i, \Omega_i, J_i, \Omega_i) \\
& \times \begin{pmatrix} J_i & J'_i & K_i \\ \Omega_i & -\Omega_i & 0 \end{pmatrix} D_{Q_i, 0}^{K_i}(\phi, \theta, 0), \tag{24}
\end{aligned}$$

and we note that it may depend on the azimuthal angle  $\phi$  in addition to the polar angle  $\theta$ . Obviously, it cannot depend on  $\gamma$ .



## B. The quasiclassical angular distribution of the fragments

Generalizing Eq. (2) we write, for linearly polarized one-photon electric dipole excitation,

$$I_{\text{class}}(\theta, \phi) \propto P_i(\theta, \phi)[1 + \beta P_2(\cos \theta)], \quad (25)$$

where  $P_i$  may depend on  $\phi$ . In Eq. (25) the  $\beta$  parameter takes, for fast dissociation, the limiting values of 2 and  $-1$  for pure parallel and perpendicular transitions, respectively. It may be modified, however, to take into account a finite dissociation time and the angular spread between the recoil direction and the transition dipole moments.<sup>17,25</sup>

Using again the Clebsch–Gordan series with  $P_2(\cos \theta) = D_{00}^2(\phi, \theta, 0)$  we obtain

$$P_2(\cos \theta) D_{Q_i 0}^{K_i} = \sum_{L, \lambda} (2L+1) \begin{pmatrix} 2 & K_i & L \\ 0 & Q_i & \lambda \end{pmatrix} \times \begin{pmatrix} 2 & K_i & L \\ 0 & 0 & 0 \end{pmatrix} D_{\lambda 0}^{L*}(\phi, \theta, 0), \quad (26)$$

from which we conclude that  $Q_i = -\lambda$ . Therefore,

$$I_{\text{class}}(\theta, \phi) \propto \sum_{L, \lambda} Y_{L\lambda}(\theta, \phi) \sum_{J_i, J'_i, \Omega_i} (-)^{J'_i - \Omega_i} (2J_i + 1)^{1/2} \times (2J'_i + 1)^{1/2} \sum_{K_i} \rho_{K_i - \lambda}^{L*}(J'_i \Omega_i, J_i \Omega_i) \times \begin{pmatrix} J_i & J'_i & K_i \\ \Omega_i & -\Omega_i & 0 \end{pmatrix} \left[ \delta_{K_i, L}(-)^\lambda + \beta(2L+1)^{1/2} (2K_i+1)^{1/2} \times \begin{pmatrix} 2 & K_i & L \\ 0 & -\lambda & \lambda \end{pmatrix} \begin{pmatrix} 2 & K_i & L \\ 0 & 0 & 0 \end{pmatrix} \right]. \quad (27)$$

The total photodissociation cross section is proportional to the  $L=0$  term in Eq. (27),

$$\sigma_{\text{class}} \propto 1 + \beta \sum_{J_i, J'_i, \Omega_i} (-)^{J'_i - \Omega_i} (2J_i + 1)^{1/2} (2J'_i + 1)^{1/2} \times \begin{pmatrix} J_i & J'_i & 2 \\ \Omega_i & -\Omega_i & 0 \end{pmatrix} \sum_{M_i} (-)^{J'_i - M_i} \begin{pmatrix} J_i & J'_i & 2 \\ M_i & -M_i & 0 \end{pmatrix} \times \langle J'_i M_i \Omega_i | \rho | J_i \Omega_i M_i \rangle. \quad (28)$$

The first term comes from the normalization of the initial angular probability  $P_i(\theta, \phi)$ . The second one is the  $L=0$  contribution of the degree to which the polarization of the light is matched or mismatched with the degree of initial alignment of the molecule's transition moment in the laboratory frame.

## IV. COMPARISON BETWEEN CLASSICAL AND QUANTUM ANGULAR DISTRIBUTIONS AND CONCLUSIONS

The main subjective objection to the use of the quasiclassical equation (2) is based on the difference between this very simple formula and the complicated quantum expression [Eq. (20)]. In fact, when expressed in terms of a sum of spherical harmonics the quasiclassical equation (27) and the

quantum equation (20) angular distributions show a striking similarity. In fact, the main difference is the double sum over  $\Omega_i$  and  $\Omega'_i$  in the quantum equation whereas in the quasiclassical expression only a single sum over  $\Omega_i$  is needed. It is then expected that if the initial state is incoherently prepared in  $\Omega_i$  the two treatments will agree with each other.

### A. Incoherently prepared $\Omega_i$ states

When  $\Omega_i$  is well defined but the system is in a coherent superposition of  $(J_i, M_i)$  states, such as the situation encountered with pendular states, we have from Eq. (20)

$$I_{\text{quant}}(\theta, \phi) \propto \sum_{L, \lambda} Y_{L\lambda}(\theta, \phi) \sum_{J_i, J'_i} (-)^{J'_i - \Omega_i} (2J_i + 1)^{1/2} \times (2J'_i + 1)^{1/2} \sigma_{\Omega_i}(J_i, J'_i) \begin{pmatrix} J_i & J'_i & K_i \\ \Omega_i & -\Omega_i & 0 \end{pmatrix} \times \left[ \delta_{K_i, L}(-)^\lambda + \beta_{\Omega_i}(J_i, J'_i) (2L+1)^{1/2} \times (2K_i+1)^{1/2} \begin{pmatrix} 2 & K_i & L \\ 0 & -\lambda & \lambda \end{pmatrix} \begin{pmatrix} 2 & K_i & L \\ 0 & 0 & 0 \end{pmatrix} \right], \quad (29)$$

with

$$\beta_{\Omega_i}(J_i, J'_i) = \frac{\sqrt{30}}{\sigma_{\Omega_i}(J_i, J'_i)} \sum_q (-)^q \begin{pmatrix} 1 & 1 & 2 \\ -q & q & 0 \end{pmatrix} M_q(J_i, \Omega_i) \times M_q^*(J'_i, \Omega_i), \quad (30)$$

which gives  $\beta=2$  for pure parallel transitions ( $q=0$ ) and  $\beta=-1$  for pure perpendicular transitions ( $q=\pm 1$ ). In the axial recoil limit, the matrix elements  $M_q(J_i, \Omega_i)$  are slowly varying functions of the total angular momentum, and so within this approximation we can neglect the dependence of these matrix elements on  $J_i$  if the number of  $J_i$  values involved in the decomposition of the initial state is not very large. In that case, Eq. (29) becomes identical to the quasiclassical equation (27). Of course, this approximate identity holds even more closely if the initial state is  $J_i$  selected for any combination of magnetic levels  $M_i$ , i.e., whatever is the polarization of the initial state. For the particular case of an initially selected  $M_i$  state this concurs with the conclusion reached by Seideman<sup>20</sup> using a different formalism.

Equation (29) is easily generalized to sum over a set of incoherently prepared  $\Omega_i$  states with their proper weighting.

### B. General initial state

As discussed before for a general linear combination of  $\Omega_i$  states, the quantum and quasiclassical expressions are similar but not identical. However, for parallel transitions  $q=q'=0$  and Eq. (20) reduces to

$$\begin{aligned}
I_{\text{quant}}(\theta, \phi) &\propto \sum_{L, \lambda} Y_{L\lambda}(\theta, \phi) \sum_{J_i, J'_i} \sum_{\Omega_i} (-)^{J'_i - \Omega_i} (2J_i + 1)^{1/2} \\
&\times (2J'_i + 1)^{1/2} M_0(J_i, \Omega_i) M_0^*(J'_i, \Omega_i) \\
&\times \sum_{K_i} \rho_{K_i \rightarrow \lambda}(J'_i \Omega_i, J_i \Omega_i) \begin{pmatrix} J_i & J'_i & K_i \\ \Omega_i & -\Omega_i & 0 \end{pmatrix} \\
&\times \left[ \delta_{K_i, L} (-)^\lambda + 2(2L + 1)^{1/2} (2K_i + 1)^{1/2} \right. \\
&\left. \times \begin{pmatrix} 2 & K_i & L \\ 0 & -\lambda & \lambda \end{pmatrix} \begin{pmatrix} 2 & K_i & L \\ 0 & 0 & 0 \end{pmatrix} \right], \quad (31)
\end{aligned}$$

which can be compared with the classical expression [Eq. (27)] with  $\beta=2$  (as it should for parallel transitions). Because the  $M_q(J_i, \Omega_i)$  matrix elements are slowly varying functions of  $J_i$  and  $\Omega_i$ , the quantum and classical expressions are identical if the number of  $J_i$  quantum numbers involved in the decomposition of the initial state is small.

On the other hand, for perpendicular transitions, in addition to the terms in Eq. (20) with  $q=q'$ , which give again a very good correspondence with the classical expression, there are additional contributions with  $\Omega'_i = \Omega_i \pm 2$ . In this case interference terms coming from coherently superimposed  $\Omega_i$  states will contribute to the angular distribution of the fragments.

## V. THE CHOICE OF THE INITIAL STATE BASIS SETS AND OTHER ANGULAR MOMENTA

In writing Eq. (9) we are implicitly considering a basis set  $(J_i, \Omega_i, M_i)$  corresponding to rotational plus electronic angular momenta. For a diatomic molecule, for instance,  $\Omega_i$  will be the projection on the body-fixed frame of the orbital plus spin electronic angular momentum for Hund's cases (a) and (c) basis sets or the orbital electronic angular momentum for a Hund's case (b) basis set in which case  $(J_i, \Omega_i)$  are replaced by  $(N_i, \Lambda_i)$ . In all cases there will be couplings (weak or strong) that mix different  $\Omega_i$  states. In addition, in many cases the coupling of the rotational angular momentum with the nuclear spin must be taken into account.

To describe rotation of polyatomic molecules, the symmetric-top eigenstates are used with  $\Omega_i$  being replaced by  $K_i$ . In the case of asymmetric tops, it is necessary to consider a sum over  $K_i$  values. In addition, for polyatomic molecules vibrational angular momenta must also be considered in the definition of the basis set.

These couplings are also operational in the final dissociative state. Provided that the separation of the photofragments is much faster than the recoupling time, these couplings may be simply taken into account by considering their effects on the initial state only. To illustrate this point, consider the case of the effect of nuclear spin on the angular distributions.

For a free molecule for which the total nuclear spin is not zero, the stationary states of the system are eigenstates of the total angular momentum  $F = J + I$ . Because the hyperfine interaction is small compared with the rotational spacing, to a very good approximation these eigenfunctions can be written as

$$\begin{aligned}
|F_i \Omega_i M_{F_i}\rangle &= \sum_{M_i, M_I} (-)^{J_i - I + M_{F_i}} (2F_i + 1)^{1/2} \\
&\times \begin{pmatrix} J_i & I & F_i \\ M_i & M_I & -M_{F_i} \end{pmatrix} |IM_I\rangle |J_i \Omega_i M_i\rangle. \quad (32)
\end{aligned}$$

If the initial state is prepared in a  $|F_i \Omega_i M_{F_i}\rangle$  state, we have  $\rho = |F_i \Omega_i M_{F_i}\rangle \langle F_i \Omega_i M_{F_i}|$ . Recall that the electric dipole transition is independent of nuclear spin, the angular distribution will be proportional to  $\rho_I = \sum_{M_I} \langle IM_I | \rho | IM_I \rangle$ , and

$$\begin{aligned}
\langle J'_i \Omega'_i M'_i | \rho_I | J_i \Omega_i M_i \rangle \\
&= \delta_{J'_i, J_i} \delta_{\Omega'_i, \Omega_i} \sum_{M_I} (2F_i + 1) \begin{pmatrix} J_i & I & F_i \\ M'_i & M_I & -M_{F_i} \end{pmatrix} \\
&\times \begin{pmatrix} J_i & I & F_i \\ M_i & M_I & -M_{F_i} \end{pmatrix}. \quad (33)
\end{aligned}$$

From Eq. (12) we then have

$$\begin{aligned}
\rho_{K_i, Q_i}(J'_i \Omega'_i, J_i \Omega_i) \\
&= \delta_{J'_i, J_i} \delta_{\Omega'_i, \Omega_i} \sum_{M_i, M'_i, M_I} (-)^{J_i - M'_i} (2K_i + 1)^{1/2} (2F_i + 1) \\
&\times \begin{pmatrix} J_i & J_i & K_i \\ M_i & -M'_i & Q_i \end{pmatrix} \begin{pmatrix} J_i & I & F_i \\ M'_i & M_I & -M_{F_i} \end{pmatrix} \\
&\times \begin{pmatrix} J_i & I & F_i \\ M_i & M_I & -M_{F_i} \end{pmatrix}. \quad (34)
\end{aligned}$$

Using Eq. (4.15) of Ref. 21 Eq. (34) can be written as

$$\begin{aligned}
\rho_{K_i, Q_i}(J'_i \Omega'_i, J_i \Omega_i) &= \delta_{Q_i, 0} \delta_{J'_i, J_i} \delta_{\Omega'_i, \Omega_i} (-)^{J_i - K_i} (2K_i + 1)^{1/2} \\
&\times (2F_i + 1) \begin{Bmatrix} F_i & F_i & K_i \\ J_i & J_i & I \end{Bmatrix} \\
&\times \begin{pmatrix} F_i & F_i & K_i \\ M_{F_i} & -M_{F_i} & 0 \end{pmatrix}. \quad (35)
\end{aligned}$$

On the other hand, if a  $|J_i \Omega_i M_i\rangle$  state is initially prepared, from Eq. (12) we have

$$\begin{aligned}
\rho_{K_i, Q_i}(J'_i \Omega'_i, J_i \Omega_i) &= \delta_{Q_i, 0} \delta_{J'_i, J_i} \delta_{\Omega'_i, \Omega_i} (-)^{J_i - M_i} (2K_i + 1)^{1/2} \\
&\times \begin{pmatrix} J_i & J_i & K_i \\ M_i & -M_i & 0 \end{pmatrix}, \quad (36)
\end{aligned}$$

and a comparison between these two expressions reveals that in the case of a hyperfine prepared initial state  $|\varphi_i\rangle = |F_i \Omega_i M_{F_i}\rangle$ , the polarization moments are reduced by the  $6-j$  symbol with respect to those of the  $|\varphi_i\rangle = |J_i \Omega_i M_i\rangle$  state. The latter is actually a linear combination of the eigenstates of the system so that in this case the angular distributions will depend on the time delay  $\Delta t$  between the preparation step and the photolysis pulse. This is the analog of depolarization by nuclear spin of molecular fluorescence. In an optical excitation scheme that takes place prior to photolysis, the molecule can be prepared by a pump pulse of duration short compared with the hyperfine period and  $J$  can be oriented or aligned with respect to the laboratory frame just as

if the nuclear spin were absent. But during the time delay between the pump and the photolysis pulse,  $\mathbf{J}$  precesses about the total angular momentum  $\mathbf{F}$  and so does the molecular axis  $\mathbf{R}$ . Hence the angular distribution must show a dependence on the time delay  $\Delta t$ . This situation is general and applies to all other cases of angular momentum couplings discussed above.

It should be noted that in the case of *adiabatically* prepared pendular states in a dc field,<sup>19,26</sup> the system is in a thermal mixture of molecule-plus-field eigenstates  $|\varphi_i\rangle = \sum J_i C_{J_i} |J_i \Omega_i M_i\rangle$ , so although there are linear combinations of  $J_i$  eigenstates there will be no dependence of the angular distribution on the time delay  $\Delta t$ .

The above treatment is quite general, and it is hoped that it will serve as a starting point in interpreting many different photodissociation experiments such as those involving molecules prepared prior to photolysis by optical excitation, static inhomogeneous and/or homogeneous electric and/or magnetic fields, as well as molecules physisorbed on solids or clusters.

Extensions of the semiclassical equation (25) can also be readily implemented: (i) circular polarized or unpolarized light in which case the  $1 + \beta P_2(\cos \theta)$  must be replaced by the corresponding expression and (ii) multiphoton photodissociation where for intermediate nonresonant transitions  $1 + \beta P_2(\cos \theta)$  should be replaced by  $1 + \beta_2 P_2(\cos \theta) + \dots + \beta_{2N} P_{2N}(\cos \theta)$ .

## ACKNOWLEDGMENTS

J.A.B. would like to thank I. Powis and P. Dagdigan for very useful correspondence on the quantum treatment and J. Vigué and B. Soep for very helpful discussions on the matter of this article. R.N.Z. would like to thank D. J. Leahy for careful and thoughtful reading of the manuscript and the U.S. National Science Foundation for support under Grant No. NSF CHE 0650414.

## APPENDIX A: A SUM INVOLVING THE SPACE-FIXED COMPONENTS OF THE ANGULAR MOMENTA

From Eqs. (10) and (11) of Ref. 27, Chap. 12, with the identification  $p=J_i, \psi=M_i, q=J, \kappa=M, r=J', \rho=M', s=J'_i, \sigma=M'_i, a=1, \alpha=\eta, b=L, \beta=-\lambda, c=1, \gamma=-\eta', d=K_i, \delta=-Q_i, x=P, \xi=-p$  we have

$$\begin{aligned} & \sum_{M_i, M'_i, M, M'} (-)^{J_i - M_i + J - M + J' - M' + J'_i - M'_i} \begin{pmatrix} J_i & 1 & J \\ M_i & \eta & -M \end{pmatrix} \\ & \times \begin{pmatrix} J & L & J' \\ M & -\lambda & -M' \end{pmatrix} \begin{pmatrix} J' & 1 & J'_i \\ M' & -\eta' & -M'_i \end{pmatrix} \\ & \times \begin{pmatrix} J'_i & K_i & J_i \\ M'_i & -Q_i & -M_i \end{pmatrix} \\ & = (-)^{2J' - J'_i - K_i - 1 - J} \sum_{P, p} (-)^{P+p} (2P+1) \begin{pmatrix} 1 & P & 1 \\ \eta & p & -\eta' \end{pmatrix} \\ & \times \begin{pmatrix} L & P & K_i \\ -\lambda & -p & -Q_i \end{pmatrix} \left\{ \begin{matrix} 1 & J_i & J \\ P & K_i & L \\ 1 & J'_i & J' \end{matrix} \right\}, \quad (\text{A1}) \end{aligned}$$

and using the symmetry properties of the  $3j$  symbols we can rewrite this equation as

$$\begin{aligned} & \sum_{M_i, M'_i, M, M'} (-)^{M' - M'_i} \begin{pmatrix} J_i & 1 & J \\ -M_i & -\eta & M \end{pmatrix} \begin{pmatrix} J & J' & L \\ M & -M' & -\lambda \end{pmatrix} \\ & \times \begin{pmatrix} J'_i & 1 & J' \\ -M'_i & -\eta' & M' \end{pmatrix} \begin{pmatrix} J_i & J'_i & K_i \\ M_i & -M'_i & Q_i \end{pmatrix} \\ & = \sum_{P, p} (-)^{K_i + J' - J'_i - 1 + \eta'} (2P+1) \begin{pmatrix} 1 & 1 & P \\ -\eta & \eta' & -p \end{pmatrix} \\ & \times \begin{pmatrix} P & K_i & L \\ p & Q_i & \lambda \end{pmatrix} \left\{ \begin{matrix} 1 & J_i & J \\ P & K_i & L \\ 1 & J'_i & J' \end{matrix} \right\}. \quad (\text{A2}) \end{aligned}$$

## APPENDIX B: AXIAL RECOIL LIMIT

Introducing  $\tilde{\Omega} = \tilde{\Omega}' = \Omega$  in Eq. (16), we obtain

$$\begin{aligned} I_{\text{quant}}(\theta, \phi) & \propto \sum_{L, \lambda} (2L+1)^{1/2} Y_{L\lambda}(\theta, \phi) \sum_{K_i, Q_i} (-)^{K_i} (2K_i+1)^{1/2} \sum_{J_i, \Omega_i, J'_i, \Omega'_i} \rho_{K_i, Q_i}(J'_i \Omega'_i, J_i \Omega_i) (2J_i+1)^{1/2} (2J'_i+1)^{1/2} \\ & \times \sum_{P, p} (2P+1)^{1/2} E_{Pp} \sum_{\Omega, q, q'} (-)^{J'_i - J_i - \Omega - 1} \begin{pmatrix} P & K_i & L \\ p & Q_i & \lambda \end{pmatrix} \sum_{J, J'} (-)^{J'} (2J+1)(2J'+1) \begin{pmatrix} J & J' & L \\ \Omega & -\Omega & 0 \end{pmatrix} \begin{pmatrix} J_i & 1 & J \\ -\Omega_i & -q & \Omega \end{pmatrix} \\ & \times \begin{pmatrix} J'_i & 1 & J' \\ -\Omega'_i & -q' & \Omega \end{pmatrix} \left\{ \begin{matrix} 1 & J_i & J \\ P & K_i & L \\ 1 & J'_i & J' \end{matrix} \right\} \langle \psi_{\Omega, \Omega}^{J_i E} | (\boldsymbol{\mu})_q | \psi_{\Omega_i, \Omega_i}^{J_i} \rangle \langle \psi_{\Omega, \Omega}^{J'_i E} | (\boldsymbol{\mu})_{q'} | \psi_{\Omega'_i, \Omega'_i}^{J'_i} \rangle^*, \quad (\text{B1}) \end{aligned}$$

and replacing  $\langle \psi_{\alpha\Omega}^{J_i E} | (\boldsymbol{\mu})_q | \psi_{\alpha_i \Omega_i}^{J_i} \rangle$ , ( $J=J_i, J_i \pm 1$ ) by  $\langle \psi_{\alpha\Omega}^{J_i E} | (\boldsymbol{\mu})_q | \psi_{\alpha_i \Omega_i}^{J_i} \rangle$  and using  $\Omega = \Omega'_i + q' = \Omega_i + q$ , we obtain



$$\begin{aligned}
I_{\text{quant}}(\theta, \phi) \propto & \sum_{L, \lambda} (2L+1)^{1/2} Y_{L\lambda}(\theta, \phi) \sum_{K_i, Q_i} (-)^{K_i} (2K_i+1)^{1/2} \sum_{J_i, \Omega_i, J'_i, \Omega'_i} \rho_{K_i, Q_i}(J'_i, \Omega'_i, J_i, \Omega_i) (2J_i+1)^{1/2} (2J'_i+1)^{1/2} \\
& \times \sum_{P, p} (2P+1)^{1/2} E_{Pp} \sum_{q, q'} (-)^{K_i - J_i + J'_i - \Omega'_i - q' - 1} \begin{pmatrix} P & K_i & L \\ p & Q_i & \lambda \end{pmatrix} \langle \psi_{\Omega_i+q, \Omega_i+q}^{J'_i E}(\boldsymbol{\mu})_q | \psi_{\Omega_i}^{J'_i} \rangle \langle \psi_{\Omega'_i+q', \Omega'_i+q'}^{J'_i E} | \\
& \times (\boldsymbol{\mu})_{q'} | i_{\Omega'_i}^{J'_i} \rangle^* S_2(J_i, J'_i, \Omega_i, \Omega'_i, q, q', P, K_i, L), \tag{B2}
\end{aligned}$$

with

$$S_2(J_i, J'_i, \Omega_i, \Omega'_i, q, q', P, K_i, L) = \sum_{J, J'} (-)^{J'} (2J+1)(2J'+1) \begin{pmatrix} J & J' & L \\ \Omega & -\Omega & 0 \end{pmatrix} \begin{pmatrix} J_i & 1 & J \\ -\Omega_i & -q & \Omega \end{pmatrix} \begin{pmatrix} J'_i & 1 & J' \\ -\Omega'_i & -q' & \Omega \end{pmatrix} \left\{ \begin{matrix} 1 & J_i & J \\ P & K_i & L \\ 1 & J'_i & J' \end{matrix} \right\}. \tag{B3}$$

From Eq. (39) of Ref. 27, Chap. 8 and the identification  $a=J'$ ,  $\alpha=-\Omega$ ,  $b=J'_i$ ,  $\beta=-\Omega'_i$ ,  $c=1$ ,  $\gamma=-q'$ ,  $d=L$ ,  $\delta=0$ ,  $e=K_i$ ,  $\epsilon=-p'$ ,  $f=P$ ,  $\varphi=p'$ ,  $g=J_i$ ,  $\eta=-\Omega_i$ ,  $j=1$ ,  $\mu=-q$ ,  $k=J$ ,  $\kappa=-\Omega$  we can write

$$\begin{aligned}
& \sum_{J, J'} (-)^{J'} (2J+1)(2J'+1) \begin{pmatrix} J'_i & 1 & J' \\ -\Omega'_i & -q' & \Omega \end{pmatrix} \begin{pmatrix} J_i & 1 & J \\ -\Omega_i & -q & \Omega \end{pmatrix} \begin{pmatrix} L & J' & J \\ 0 & -\Omega & \Omega \end{pmatrix} \left\{ \begin{matrix} 1 & J'_i & J' \\ P & K_i & L \\ 1 & J_i & J \end{matrix} \right\} \\
& = \sum_{p'} (-)^{J_i+1-L} \begin{pmatrix} K_i & P & L \\ -p' & p' & 0 \end{pmatrix} \begin{pmatrix} K_i & J'_i & J_i \\ -p' & -\Omega'_i & \Omega_i \end{pmatrix} \begin{pmatrix} P & 1 & 1 \\ p' & -q' & q \end{pmatrix}, \tag{B4}
\end{aligned}$$

which using the symmetry properties of the  $3-j$  and  $9-j$  symbols provides

$$S_2(J_i, J'_i, \Omega_i, \Omega'_i, \Omega, q, q', P, K_i, L) = \sum_{p'} (-)^{K_i+1+J_i} \begin{pmatrix} P & K_i & L \\ -p' & p' & 0 \end{pmatrix} \begin{pmatrix} J_i & J'_i & K_i \\ \Omega_i & -\Omega'_i & -p' \end{pmatrix} \begin{pmatrix} 1 & 1 & P \\ -q & q' & -p' \end{pmatrix}. \tag{B5}$$

Using this result into Eq. (B2), Eq. (18) is obtained.

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