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The parity-adapted basis set in the formulation of the photofragment angular momentum polarization problem: The role of the Coriolis interaction

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We present a theoretical framework for calculating the recoil-angle dependence of the photofragment angular momentum polarization taking into account both radial and Coriolis nonadiabatic interactions in the diatomic/linear photodissociating molecules. The parity-adapted representation of the total molecular wave function has been used throughout the paper. The obtained full quantum-mechanical expressions for the photofragment state multipoles have been simplified by using the semiclassical approximation in the high-J limit and then analyzed for the cases of direct photodissociation and slow predissociation in terms of the anisotropy parameters. In both cases, each anisotropy parameter can be presented as a linear combination of the generalized dynamical functions $f_K(q,q',\tilde{q},\tilde{q}')$ of the rank K representing contribution from different dissociation mechanisms including possible radial and Coriolis nonadiabatic transitions, coherent effects, and the rotation of the recoil axis. In the absence of the Coriolis interactions, the obtained results are equivalent to the earlier published ones. The angle-recoil dependence of the photofragment state multipoles for an arbitrary photolysis reaction is derived. As shown, the polarization of the photofragments in the photolysis of a diatomic or a polyatomic molecule can be described in terms of the anisotropy parameters irrespective of the photodissociation mechanism. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2919130]

I. INTRODUCTION

Investigation of the recoil-angle dependence of the spin and orbital angular momentum polarizations of the products of photochemical reactions has received considerable attention as a means to obtain detailed information on the photodissociation dynamics.[1–3] In particular, the study of the electronic angular momentum polarization of atomic photofragments is now widely used as a tool for direct probing of the electronic structure of the reaction complex, coherent effects and nonadiabatic interactions between different reactive potential energy surfaces (PESs).[4–16]

The nonadiabatic interactions occurring in the slow atomic collisions and in photodissociation of linear molecules can be in general separated into two groups:[17,18] (i) homogeneous (radial) interactions which preserve the projection of the molecular angular momentum Ω onto the recoil axis and (ii) inhomogeneous (Coriolis) interactions between the electronic and nuclear degrees of freedom which change the projection Ω.

The radial nonadiabatic interactions are known to be more important than the Coriolis interactions at relatively high kinetic energies of the photofragments when a dissociating molecule has no time to rotate during the photochemical event which is described well by the axial recoil approximation. Most of the theoretical approaches developed for a number of years for understanding in this area[8,9,19–25] have been built upon the foundation established by Siebbeles *et al.*[5] based on the expression for the recoil-angle dependence of the fragment state multipoles by using the axial recoil approximation, where the role of the Coriolis interaction has been neglected. The important advantage of these approaches is that they allow for the complete separation of the kinematical part and the angular momentum independent dynamical functions from each other. Therefore, these expressions can in many cases be used for the analysis of the dynamical processes in photodissociation and for interpretation of the experimental data without actual computing of the set of closed coupling equations.

However, the Coriolis interactions may become important at relatively low kinetic energies when the curvilinearity of the fragment trajectory has to be taken into consideration, particularly in the case of the near-threshold photodissociation and in the case of the predissociation.

The main goal of this paper is to develop and analyze the complete quantum-mechanical expressions of the recoil-angle dependence of the photofragment orientation and alignment which take into account both radial and Coriolis nonadiabatic interactions as well as the full range of coherent effects. For overcoming the axial recoil approximation, we used the quasiclassical approach recently developed by Kuznetsov and Vasyutinskii;[26] however, unlike the *parity-unadapted* presentation of the molecular wave function used by Kuznetsov and Vasyutinskii,[26] the *parity-adapted* presentation has been used throughout this paper.

As known,[17,18,27–30] the parity-adapted presentation of the molecular wave function which explicitly introduces the molecular total parity μ has an undoubted advantage because it allows for the separation of the set of the closed-coupled equation in the scattering theory into two blocks relating to

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the $\mu=+1$ and $\mu=-1$ values, thus simplifying the computation of the photodissociation problem. However, the application of the parity-adapted presentation of the molecular wave function in many cases is not *necessary* for solving the molecular dynamics problems. In their recent paper Kuznetsov and Vasyutinskii[31] suggested that the expansion of the total excited state scattering wave function $\Psi^{-(\hat{\mathbf{k}},j,m)}(\mathbf{R},\mathbf{r},E)$ can be done by using *any* set of orthogonal wave functions which depends on the recoil vector $\hat{\mathbf{k}}$, incoming vector $\mathbf{R}/R$, and the electronic coordinates $\mathbf{r}$ and that the choice of a particular orthogonal basis set is mostly determined only by the convenience of its practical use.

Therefore, the second goal of this paper was to carry out a formal mathematical proof of equivalence of the approaches using the parity-adapted and parity-unadapted basis sets in order to make a formal proof of the validity of the parity-unadapted approaches used in the field until now.[5,8,9,19,21–25]

As shown by Balint-Kurti and Shapiro[27,28] and by Siebbeles *et al.*[4] some years ago, the general expression for the photodissociation cross section can be relatively easily written in the parity-adapted form. However, to the best of our knowledge, the final expressions for the recoil-angle dependence of the fragment state multipoles have never been presented until now by using the parity-adapted basis in the form convenient for analyzing the experimental data.

The approach used in this paper bases upon the results of the previous papers by Kuznetsov and Vasyutinskii[26,31] where the *adiabatic* body frame electronic wave function representation has been used; however, instead of the quantum number Ω in Refs. 26 and 31, in this paper, the quantum numbers $\lambda=|\Omega|$ and μ have been used. The advantage of this representation is that the total parity μ is always preserved in the molecular excited state, while the quantum number λ is preserved in the absence of the Coriolis interactions.

Within the (λ,μ) representation of the molecular wave function, the fully quantum expression for the photofragment state multipoles have been explicitly derived from the scattering wave function formalism. The set of closed-coupled equations in the (λ,μ) representation has also been derived and the interaction matrix elements corresponding to the radial and Coriolis nonadiabatic interactions between different PESs have been analyzed.

The expression for the photofragment state multipoles was simplified using the quasiclassical approximation[26] and summation over all possible angular momentum values J,J' has been proceeded in the high-J limit. The obtained expressions were found to be *exactly equivalent* to the expressions obtained in the (Ω) representation in Ref. 26. This founding provides the formal proof of the parity-unadapted presentation of the molecular wave function used before.

The expressions for the photofragment state multipoles have been analyzed. They contain the generalized dynamical functions of the rank K, $f_K(q,q',\tilde{q},\tilde{q}')$, which depend on the photodissociation dynamics, including probabilities of the radial and Coriolis nonadiabatic transitions, and the phase difference between different dissociation channels. In general, the generalized dynamical functions are characterized by four indices $q,q',\tilde{q},\tilde{q}'$, which describe the symmetry of the radiative transitions from the initial state of the parent molecule to the excited state and the following nonadiabatic processes. If the Coriolis nonadiabatic interactions can be neglected, the indices $\tilde{q}$ and $\tilde{q}'$ are equal to the indices q and q', respectively, and the generalized dynamical functions $f_K(q,q',\tilde{q},\tilde{q}')$ become equivalent to the dynamical functions $f_K(q,q')$ introduced elsewhere.[5,21]

For this case the angle-recoil distributions of the photofragment state multipoles have been tabulated in terms of the anistropy parameters β, α_K, γ_K, γ'_K, η_K, and s_K, of the rank $K=0,\ldots 4$ which were defined as normalized linear combinations of the dynamical functions $f_K(q,q')$ of the same rank.[8,32–34] This paper shows that in the case if the Coriolis nonadiabatic interactions are important, the photofragment angle-recoil distribution can still be expressed in terms of the anisotropy parameters. Each parameter can be written as a linear combination of the generalized dynamical functions representing contribution from different dissociation mechanism, including possible radial and Coriolis nonadiabatic transitions between PESs, coherent effects, and the rotation of the recoil axis. However, in general the anisotropy parameters cannot be classified in accordance with their "parallel", or "perpendicular" character. In general, each anisotropy parameter can be classified in accordance with the values of the photofragment rank K, the rank of the light polarization matrix k_d, and their projection q_k onto the *asymptotic recoil direction*.

The expressions for the anisotropy parameters of the rank $K=0,1,2$ have been analyzed for the cases of direct photodissociation and predissociation, and several new dissociation mechanisms resulting in production of oriented and aligned photofragments have been discussed. In particular, it was shown that the Coriolis interaction can induce production of the fragment orientation $(K=1)$ even in case of a pure parallel radiative transition in the parent molecule.

We also present a general expression describing the photolysis of an isotropic ensemble of molecules and show that the recoil-angle dependence of the photofragment angular momentum polarization has the same universal form for *any* photodissociation process in a diatomic or polyatomic molecule within the first-order time-dependent perturbation theory, including direct dissociation and predissociation. The recoil-angle dependence is presented in terms of the *anisotropy-transforming coefficients* $\mathbf{c}^K_{k_d q_k}$ which are simply proportional to the corresponding anisotropy parameters β, α_K, γ_K, γ'_K, η_K, s_K in pairs. However, the particular expressions for the anisotropy parameters depend on the photodissociation mechanism.

The paper is organized as follows. The formal theory using the parity-adapted representation of the molecular wave function is given in Sec. II. This section contains the expansion of the dissociative wave function over the parity-adapted basis set, derivation of the scattering equations, and the general expression for the photodissociation polarization cross section. Simplification of the obtained general expression using the quasiclassical approximation is given in Secs. III and IV. These sections contain derivation and analysis of the expressions for the fragment angular momentum polarization in the cases of fast dissociation and slow predissociation as well as analysis of expressions for the anisotropy parameters taking into consideration both radial and Coriolis nonadiabatic interactions. Section V contains the expressions describing the photolysis of an arbitrary molecule and their discussion. The calculation details are given in the Appendixes.

II. GENERAL FORMALISM

A. Photodissociation cross section

We consider the photodissociation of a molecule AB producing the fragments A and B with angular momenta j_A and j_B, respectively. The projection of the angular momentum $\mathrm{j_A}$ onto the laboratory axis $\mathbf{Z}$ is m_A and the projection of the angular momentum j_B onto this axis is m_B.

The generalized photofragmentation cross section $\sigma(\hat{\mathbf{k}},E;\tilde{n},\tilde{n}')$ describing the distribution of the fragment angular momenta j_A and j_B along the recoil direction $\hat{\mathbf{k}}(\theta_k,\phi_k)$ can be presented in the following universal form:[21,27,28]

$$\sigma(\hat{\mathbf{k}},E;\tilde{n}',\tilde{n}) = \frac{C}{(2J_i+1)}\sum_{M_i}\langle\Psi^{-(\hat{\mathbf{k}},\tilde{n}')}(\mathbf{R},\mathbf{r}_i,E)|\hat{\mathbf{d}}\cdot\mathbf{e}|\Psi_{J_iM_i}\rangle \times\langle\Psi^{-(\hat{\mathbf{k}},\tilde{n})}(\mathbf{R},\mathbf{r}_i,E)|\hat{\mathbf{d}}\cdot\mathbf{e}|\Psi_{J_iM_i}\rangle^*, \tag{1}$$

where $\mathbf{e}$ is a light polarization vector, $\hat{\mathbf{d}}$ is a molecular transition dipole moment operator, $\mathbf{R}$ is the vector connecting the centers of mass of the fragments, $E=E_i+\hbar\omega$ is the total photofragment energy, ω is the frequency of the incident light, $\mathbf{r}_i$ denotes collectively all internal coordinates of the fragments, and C is a constant: $C=(\pi\omega)/(c\epsilon_o)$.

The wave function $\Psi_{J_iM_i}\equiv\Psi_{J_iM_i}(\mathbf{R},\mathbf{r}_i,E_i)$ in Eq. (1) describes the initial state of the parent molecule, where J_i and M_i are the total molecular angular momentum and its Z projection, respectively. In this paper, the initial state is assumed to have an isotropic distribution of the angular momenta $\mathbf{J}_i$ resulting in the condition $J_i=J_i'$, $M_i=M_i'$ in Eq. (1); however, the obtained results can be readily generalized to the case of an anisotropic initial state of the parent molecule. The dissociative wave function $\Psi^{-(\hat{\mathbf{k}},\tilde{n})}(\mathbf{R},\mathbf{r}_i,E)$ in Eq. (1) describes the evolution of the excited electronic molecular state. It is in general a complicated function of the molecular coordinates and the vectors $\mathbf{R}/R$ and $\hat{\mathbf{k}}$.[35] In the asymptotic region, $R\to\infty$, this function describes two photofragments flying apart with total energy E in a direction specified by the unit vector $\hat{\mathbf{k}}$ with polar angles θ,ϕ. The index $\tilde{n}$ is the set of quantum numbers specifying the electronic states and angular momenta (j_A,m_A,j_B,m_B) of the fragments. Assuming that the angular momentum polarization of only fragment A is detected, we will further average the polarization cross section $\sigma(\hat{\mathbf{k}},E;\tilde{n}',\tilde{n})$ over the j_B, m_B states of fragment B.

The diagonal elements of the photodissociation cross section $\sigma(\hat{\mathbf{k}},E;\tilde{n}',\tilde{n})$ with $\tilde{n}'=\tilde{n}$ are conventional photofragmentation cross sections. The off-diagonal matrix elements with $\tilde{n}'\neq\tilde{n}$ describe the coherence between different photofragment A quantum states which have been the subject of many recent important theoretical and experimental investigations.[5,6,36] Equation (1) describes a steady state regime of the molecular photodissociation by the monochromatic light with frequency ω. This approach nicely fits typical experimental conditions if nanosecond laser pulses are used.

Following the procedure recently used by Balint-Kurti *et al.*,[21] it is convenient to change in the right part of Eq. (1) from the j_A,m_A,j_B,m_B basis to the j_A,j_B,j,m basis, where j and m are the total photofragment angular momentum $\mathbf{j}=\mathbf{j}_A+\mathbf{j}_B$ and its Z projection, respectively. Then, after averaging over the j_B,m_B states of fragment B, transforming the cross section in the left part of Eq. (1) from the j_A,m_A,j_A,m_A' representation to the irreducible KQ representation using the relation[29,37]

$$\sigma^{j_A}_{KQ}(\theta,\phi) = \sum_{m_A',m_A}(-1)^{j_A-m_A}(2K+1)^{1/2} \times\begin{pmatrix} j_A & j_A & K \\ m_A & -m_A' & -Q\end{pmatrix}\sigma^{j_A}_{m_A'm_A}(\theta,\phi), \tag{2}$$

proceeding summation over the indices m_A,m_A', and $m_B=m_B'$, the photodissociation cross section describing the angular momentum polarization of photofragment A can be presented in the form[26]

$$\sigma^{(j_A)}_{KQ}(\hat{\mathbf{k}}) = \frac{C}{2J_i+1}\sum_{M_i,j_B}\sum_{j',m',j,m}(-1)^{j_A+j_B+j+K-Q} \times[(2K+1)(2j+1)]^{1/2}C^{j'm'}_{jmK-Q} \times\begin{Bmatrix} j_A & j_A & K \\ j' & j & j_B\end{Bmatrix}\langle\Psi^{-(\hat{\mathbf{k}},j',m')}(\mathbf{R},\mathbf{r}_i,E) \times|\hat{\mathbf{d}}\cdot\mathbf{e}|\Psi_{J_iM_i}\rangle\langle\Psi^{-(\hat{\mathbf{k}},j,m)}(\mathbf{R},\mathbf{r}_i,E)|\hat{\mathbf{d}}\cdot\mathbf{e}|\Psi_{J_iM_i}\rangle^*, \tag{3}$$

where $C^{j'm'}_{jmK-Q}$ is a Clebsch–Gordan coefficient and the term in the square brackets is a 6-j symbol.[29]

The index K in Eq. (3) is the photofragment rank which is always positive and limited to the integer values from the interval $0,\ldots,2j_A$. The index Q is the projection of the rank K, $-K\leqslant Q\leqslant K$. Expression for the state multipole $\sigma^{(j_A)}_{KQ}(\theta_k,\phi_k)$ in Eq. (3) is a basic one which will be later transformed and simplified.

B. Expansion of the dissociative wave function over the parity-adapted basis set

The dissociative wave function $\Psi^{-(k,j,m)}(\mathbf{R},\mathbf{r}_i,E)$ in Eq. (3) is well known in the collision theory.[17,35,38] It is a solution of the time independent Schrödinger equation for the electronic molecular excited state at all interfragment distances $0<R<\infty$. In the case of the photodissociation, this function obeys usual boundary condition in the infinity corresponding to an outgoing plane wave in the channel with a specific internal state and incoming spherical waves in all other possible open channels:[28]

$$\Psi^{-(\hat{\mathbf{k}},jm)}(\mathbf{R},\mathbf{r}_i,E) \overset{R\to\infty}{\sim} e^{i\hat{\mathbf{k}}\mathbf{R}}|jm\rangle + \sum_{j'm'} \frac{k'_{j'}}{k_j} f_{j'm';jm}(\hat{\mathbf{k}};\mathbf{R}) \frac{e^{-ik'_{j'}R}}{R}|j'm'\rangle, \tag{4}$$

where k_j, $k'_{j'}$ are wavevectors, and the additional quantum numbers, except j and m, which describe the photofragment internal states $(j_1, j_2, \ldots)$, are not written for brevity.

For any interfragment distance R, the dissociative wave function $\boldsymbol{\Psi}^{-(\hat{\mathbf{k}},j,m)}(\mathbf{R},\mathbf{r}_i,E)$ can in general be expanded over a set of orthogonal wave functions which depend on two vectors $\hat{\mathbf{k}}$ and $\mathbf{R}/R$ and on all electronic coordinates $\mathbf{r}_i$. The choice of a particular orthogonal basis set is usually determined by the convenience of its practical use. Particularly, a convenient basis set contains the excited state wave functions in the total angular momentum representation:[17]

$$\Psi^{JM}_{n\Omega} = \sqrt{\frac{2J+1}{4\pi}} D^{J*}_{M\Omega}(\phi,\theta,0)|n\Omega\rangle, \tag{5}$$

where $D^{J*}_{M\Omega}(\phi,\theta,0) \equiv D^{J*}_{M\Omega}(\hat{\mathbf{R}},0)$ is a Wigner D function,[29] $|n\Omega\rangle \equiv \Psi_{n\Omega}(R,\mathbf{r}_i)$ is a body frame adiabatic electronic wave function, and M and Ω are the projections of the total molecular angular momentum J onto the laboratory axis Z and onto the internuclear axis, respectively. n is an additional quantum number (channel number).

The wave functions $|n\Omega\rangle$ are the eigenfunctions of the molecular electronic Hamiltonian $\hat{\mathcal{H}}_e = \hat{\mathcal{H}}_0 + \hat{V}_{AB}$, where $\hat{\mathcal{H}}_0$ is the Hamiltonian of the free fragments and $\hat{V}_{AB}$ is the interaction. This basis set was first used for treating the problem of photofragment angular momentum polarization by Siebbeles *et al.*[5] and was later used by many other authors elsewhere.[8,13,21,26,31] The molecular wave functions $\Psi^{JM}_{n\Omega}$ in Eq. (5) are convenient for solving the problems related to diatomic/linear molecules because the quantum numbers n and Ω are preserved in many basic photodissociation processes. Particularly, the quantum number n is preserved in adiabatic dissociation along one potential curve, while the quantum number Ω is preserved in the absence of the Coriolis-type nonadiabatic interactions. As a result, the polarization of the photofragment angular momenta can be calculated in many important simple cases without referring to the set of scattering equations which greatly simplifies the analysis and allows us to establish the connection between the detailed physics of the dissociation process and the experimental observations (see the review papers in Refs. 13, 14, and 16).

However, the *total parity* $\mu = \pm 1$ under inversion of all electron and nuclear coordinates in the origin is not incorporated into the expression for the molecular wave functions in Eq. (5). As known, the total parity is preserved in molecular dynamics problems which results in separation of the set of the closed-coupled equations into two independent subsets.[17,27,35] Moreover, incorporation of the total parity seems to be important to address the problem of the Coriolis interaction and the problem of the angular momentum polarization of the products of photolysis of polyatomic molecules. For a linear parent molecule, it is convenient to define the parity-adapted molecular wave function as

$$\Psi^{JM\mu}_{n\lambda} = t_\lambda \sqrt{\frac{2J+1}{4\pi}} (D^{J*}_{M\lambda}(\hat{\mathbf{R}},0)|n\lambda\rangle + \mu(-1)^{J-\varphi} D^{J*}_{M-\lambda}(\hat{\mathbf{R}},0)|n-\lambda\rangle), \tag{6}$$

where $\lambda = |\Omega|$ is the modulus of the projection of total angular momentum on the molecular axis and t_λ is a normalization factor, $t_\lambda = 1/\sqrt{2}$ if $\lambda \neq 0$ and $t_\lambda = 1/2$ if $\lambda = 0$.

Using the symmetry of the Wigner D functions and having in mind that the transformation of the body frame coordinates by the inversion operator $\hat{I}$ is equivalent to the reflection in the plane containing the molecular axis,[29] one can show that the behavior of the wave function $\Psi^{JM\mu}_{n\lambda}$ in Eq. (6) under inversion of all electron and nuclear coordinates in the origin is described by

$$\hat{I}\Psi^{JM\mu}_{n\lambda} = \mu \Psi^{JM\mu}_{n\lambda}. \tag{7}$$

In the case $\lambda \neq 0$, the $\mu = \pm 1$ wave functions in Eq. (6) result in two opposite parity states for each J value. In the case $\lambda = 0$, the parity index in Eq. (6) is equal to

$$\mu = (-1)^{J-\varphi} \tag{8}$$

and results in a certain parity state for each J value.

The phase factor $(-1)^{\varphi}$ in Eqs. (6) and (8) is determined by the behavior of the body frame adiabatic electronic wave function $|n\lambda\rangle$ under reflection $\hat{\sigma}_v$ of all internal coordinates in the molecular xz plane (we assume that the body frame z axis is parallel to the molecular axis):

$$\hat{\sigma}_v|n\lambda\rangle = (-1)^{\varphi-\lambda}|n-\lambda\rangle. \tag{9}$$

The phase factor $(-1)^{\varphi}$ can be found by expanding the molecular electronic wave function $|n\lambda\rangle$ over the free fragment wave functions of an incoming channel in the asymptotic area:[39,40]

$$|n\lambda\rangle \overset{R\to\infty}{\sim} \sum_{\Omega'_A\Omega'_B} \mathcal{T}^{n\lambda}_{j'_A\Omega'_A j'_B\Omega'_B} |j'_A\Omega'_A\rangle |j'_B\Omega'_B\rangle, \tag{10}$$

where the expansion coefficients $\mathcal{T}^{n\lambda}_{j'_A\Omega'_A j'_B\Omega'_B}$ depend on the fragment angular momenta j'_A, j'_B and on the type of the long-range interaction between the fragments. Due to the axial symmetry of the molecule, the coefficients $\mathcal{T}^{n\lambda}_{j'_A\Omega'_A j'_B\Omega'_B}$ obey the selection rule $\lambda = \Omega'_A + \Omega'_B$. In general, they are not the Clebsch–Gordan coefficients and should be calculated by using the perturbation theory methods. The calculated values of these coefficients for many important particular cases are tabulated in Refs. 16 and 40.

If $\lambda \neq 0$, the coefficients $\mathcal{T}^{n\lambda}_{j'_A\Omega'_A j'_B\Omega'_B}$ follow the symmetry rule[16]

$$\mathcal{T}^{n-\lambda}_{j'_A-\Omega'_A j'_B-\Omega'_B} = \mathcal{T}^{n\lambda}_{j'_A\Omega'_A j'_B\Omega'_B} \tag{11}$$

and the molecular wave function $|n\lambda\rangle$ in the left part of Eq. (10) behaves under reflection $\hat{\sigma}_v$ exactly in the same way as the product of two free fragment wave functions in the right part of Eq. (10). In this case, the phase factor is equal to

$(-1)^{\varphi}=(-1)^{j'_A+j'_B}p'_A p'_B$, where p'_A and p'_B are the parities of the free fragment states in an incoming channel.

If $\lambda=0$, the coefficients $\mathcal{T}^{n0}_{j'_A\Omega'_A j'_B\Omega'_B}$ follow the symmetry rule[16]

$$\mathcal{T}^{n0}_{j'_A-\Omega'_A j'_B-\Omega'_B}=(-1)^{j'_A+j'_B-j'}\mathcal{T}^{n0}_{j'_A\Omega'_A j'_B\Omega'_B}, \tag{12}$$

where j' is the total fragment angular momentum, $\mathbf{j}'=\mathbf{j}'_A+\mathbf{j}'_B$, which in this case can be only integer. The phase factor is equal to $(-1)^{\varphi}=(-1)^{j'}p'_A p'_B$ and results in the Σ^+ or Σ^- molecular states when $(-1)^{\varphi}=+1$ or $(-1)^{\varphi}=-1$, respectively.

The parity-adapted molecular wave function $\Psi^{JM\mu}_{n\lambda}$ can be presented in the form in Eq. (6) for either integer or half-integer values of the total angular momentum J where the phase $(J-\varphi)$ is always integer. The quantum numbers J, M, and μ are all preserved in the molecular dynamics problems as they commute with the molecular Hamiltonian. The functions $\Psi^{JM\mu}_{n\lambda}$ form a complete orthogonal basis set which is used in this paper for expanding the dissociative wave functions $\Psi^{-(\hat{\mathbf{k}},j,m)}(\mathbf{R},\mathbf{r}_i,E)$ in Eq. (2). An appropriate form of this expansion is (see Appendix A)

$$\Psi^{-(\hat{\mathbf{k}},j,m)}(\mathbf{R},\mathbf{r}_i,E)=\frac{1}{R}\sum_{J,M,\mu}\sum_{\lambda_R,\lambda_k}\sum_{n_R n_k}e^{i(\pi/2)J}\chi^{J\mu}_{n_R\lambda_R;n_k\lambda_k}(R)$$
$$\times\Psi^{JM\mu}_{n_R\lambda_R}(\mathbf{R},\mathbf{r}_i,R)\Phi^{JM\mu}_{jmn_k\lambda_k}(\hat{\mathbf{k}}), \tag{13}$$

where the subscript indices R and k are related to the incoming and outgoing channels, respectively. The wave function in the outgoing channel, $\Phi^{JM\mu}_{jmn_k\lambda_k}(\hat{\mathbf{k}})$ in Eq. (13) is given by

$$\Phi^{JM\mu}_{jmn_k\lambda_k}(\hat{\mathbf{k}})=\sum_{\Omega_A\Omega_B}\sqrt{\frac{2J+1}{4\pi}}D^{J}_{M\Omega_k}(\hat{\mathbf{k}},0)D^{j*}_{m\Omega_k}(\hat{\mathbf{k}},0)$$
$$\times C^{j\Omega_k}_{j_A\Omega_A j_B\Omega_B}t_{\lambda}[(\mathcal{T}^{n_k\lambda_k}_{j_A\Omega_A j_B\Omega_B})^*$$
$$+\mu(-1)^{J-\varphi_k}(\mathcal{T}^{n_k-\lambda_k}_{j_A\Omega_A j_B\Omega_B})^*], \tag{14}$$

where the relationship $\Omega_k=\Omega_A+\Omega_B$ is fulfilled due to the symmetry properties of the Clebsch–Gordan coefficient $C^{j\Omega_k}_{j_A\Omega_A j_B\Omega_B}$. The phase factor $(-1)^{\varphi_k}$ in Eq. (14) is equal to $(-1)^{\varphi_k}=(-1)^{j_A+j_B}p_A p_B$ if $\lambda_k\neq 0$ and $(-1)^{\varphi_k}=(-1)^{j}p_A p_B$ if $\lambda_k=0$, where the quantum numbers j_A, j_B, j, p_A, and p_B refer to the outgoing channel.

The expansion coefficients $\chi^{J\mu}_{n_R\lambda_R;n_k\lambda_k}(R)$ in Eq. (13) are radial scattering wave functions which obey the following asymptotic boundary conditions:

$$\chi^{J\mu}_{n_R\lambda_R;n_k\lambda_k}(R)\overset{R\to\infty}{\sim}-\frac{4\pi^2 i}{\sqrt{kk'}}[\delta_{\lambda_R,\lambda_k}\delta_{n_k,n_R}e^{i(kR-(\pi/2)J)}$$
$$-S^{J\mu}_{n_R\lambda_R n_k\lambda_k}e^{-i(k'R-(\pi/2)J)}] \tag{15}$$

for open channels and

$$\chi^{J\mu}_{n_R\lambda_R;n_k\lambda_k}(R)\overset{R\to\infty}{\sim}0$$

for closed channels.

The term $S^{J\mu}_{n_R\lambda_R n\lambda_k}$ in Eq. (15) is a scattering matrix in the $(Jn\lambda\mu)$ representation,[17] while k and k' are the wavevectors in the n and n_R channels, respectively. The parity-adapted expansion of the dissociative wave function $\Psi^{-(\hat{\mathbf{k}},j,m)}(\mathbf{R},\mathbf{r}_i,E)$ in Eq. (13) has been directly derived from the expansion in Eq. (5) in the paper of Kuznetsov and Vasyutinskii[26] where the parity was not incorporated. The relationship between the parity-adapted radial scattering wave functions $\chi^{J\mu}_{n_R\lambda_R;n_k\lambda_k}(R)$ in Eqs. (13)–(15) and the parity-unadapted radial scattering wave functions $\chi^{J}_{n_R\Omega_R;n_k\Omega_k}(R)$ used in Ref. 26 is as follows:

$$\chi^{J\mu}_{n_R\lambda_R;n_k\lambda_k}(R)=t_{\lambda_R}t_{\lambda_k}[\chi^{J}_{n_R\lambda_R;n_k\lambda_k}(R)$$
$$+(-1)^{J-\varphi_R}\mu\chi^{J}_{n_R-\lambda_R;n_k\lambda_k}(R)$$
$$+(-1)^{J-\varphi_k}\mu\chi^{J}_{n_R\lambda_R;n_k-\lambda_k}(R)$$
$$+(-1)^{\varphi_k-\varphi_R}\chi^{J}_{n_R-\lambda_R;n_k-\lambda_k}(R)]. \tag{16}$$

Using the symmetry of the radial wave function $\chi^{J}_{n_R\lambda_R;n_k\lambda_k}(R)$ which follows from the time reversal:[41]

$$\chi^{J}_{n_R\lambda_R;n_k\lambda_k}(R)=(-1)^{\varphi_k-\varphi_R}\chi^{J}_{n_R-\lambda_R;n_k-\lambda_k}(R), \tag{17}$$

Eq. (16) can be simplified to the form

$$\chi^{J\mu}_{n_R\lambda_R;n_k\lambda_k}(R)=2t_{\lambda_R}t_{\lambda_k}[\chi^{J}_{n_R\lambda_R;n_k\lambda_k}(R)$$
$$+(-1)^{J-\varphi_R}\mu\chi^{J}_{n_R-\lambda_R;n_k\lambda_k}(R)]$$
$$=2t_{\lambda_R}t_{\lambda_k}[\chi^{J}_{n_R\lambda_R;n_k\lambda_k}(R)$$
$$+(-1)^{J-\varphi_k}\mu\chi^{J}_{n_R\lambda_R;n_k-\lambda_k}(R)]. \tag{18}$$

The radial scattering wave functions $\chi^{J\mu}_{n_R\lambda_R;n_k\lambda_k}(R)$ in Eqs. (16) and (18) are the subject of a set of scattering (closed-coupled) equations in the $(Jn\lambda\mu)$ representation which will be presented in the next section.

C. Scattering equations in the $(Jn\lambda\mu)$ representation

The scattering equations in the $(Jn\lambda\mu)$ representation can be obtained in the usual way by substituting the dissociative wave function $\Psi^{-(\hat{\mathbf{k}},j,m)}(\mathbf{R},\mathbf{r}_i,E)$ in Eq. (13) into the Schrödinger equation

$$\hat{\mathcal{H}}\Psi^{-(\hat{\mathbf{k}},j,m)}=E\Psi^{-(\hat{\mathbf{k}},j,m)}, \tag{19}$$

by multiplying Eq. (19) from the left with $\Psi^{JM\mu}_{n_R\lambda_R}(\mathbf{R},\mathbf{r}_i,R)\Phi^{JM\mu}_{jmn_k\lambda_k}(\hat{\mathbf{k}})$ and by integrating over all electron and nuclear variables.

The total molecular Hamiltonian $\hat{\mathcal{H}}$ in Eq. (19) consists of electronic and nuclear parts:

$$\hat{\mathcal{H}}=\hat{\mathcal{H}}_e-\frac{1}{2\mu_f R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)+\frac{1}{2\mu_f R^2}(\hat{\mathbf{J}}-\hat{\mathbf{j}})^2, \tag{20}$$

where μ_f is the fragment reduced mass and $\hat{\mathbf{J}}$ and $\hat{\mathbf{j}}$ are the total molecular angular momentum operator and total electron angular momentum operator, respectively. Using unitary and orthogonality properties of the basis wave functions $\Psi^{JM\mu}_{n_R\lambda_R}(\mathbf{R},\mathbf{r}_i,R)$ and $\Phi^{JM\mu}_{jmn_k\lambda_k}(\hat{\mathbf{k}})$, the set of scattering equations in the $(Jn\lambda\mu)$ representation can be presented as (see Appendix B)

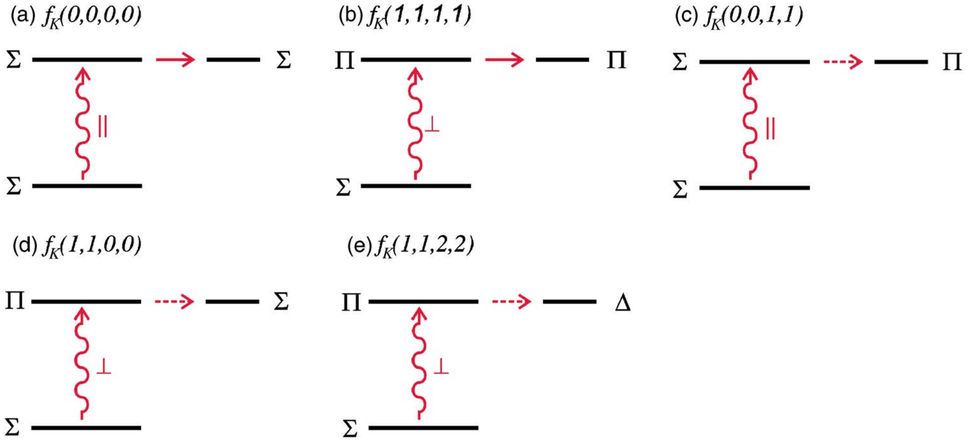

FIG. 1. (Color online) [(a)–(e)] Examples of dissociation mechanisms resulting in single final states via noncoherent optical excitation of the parent molecule. The terms $f_k(q,q',\tilde{q},\tilde{q}')$ in each figure are generalized dynamical functions which describe the corresponding dissociation mechanisms. The wavy lines marked ∥ and ⊥ indicate parallel and perpendicular optical transitions, respectively. The solid and dashed straight lines indicate radial and Coriolis nonadiabatic transitions, respectively. The above dissociation mechanisms can contribute to the anisotropy parameters β, α_K, and s_K.

$$\left(-\frac{1}{2\mu_f}\frac{d^2}{dR^2}+U_{n_R\lambda_R}(R)-E+\frac{J(J+1)-\lambda_R^2}{2\mu_f R^2}\right)\chi^{J\mu}_{n_R\lambda_R n_k\lambda_k}$$
$$=\sum_{n'_R,\lambda'_R}[\hat{V}^R_{n_R\lambda_R n'_R\lambda'_R}\chi^{J\mu}_{n'_R\lambda'_R n_k\lambda_k}+\hat{V}^C_{n_R\lambda_R n'_R\lambda'_R}\chi^{J\mu}_{n'_R\lambda'_R n_k\lambda_k}], \quad (21)$$

where $U_{n_R\lambda_R}(R)$ is the electronic potential energy and $\hat{V}^R_{n_R\lambda_R n'_R\lambda'_R}$ and $\hat{V}^C_{n_R\lambda_R n'_R\lambda'_R}$ are the matrix elements of the radial and Coriolis interaction operators, respectively.

In general, the set of the closed-coupled equations in Eq. (21) contains two independent sets of equations with respect to the two possible values of the parity index $\mu=\pm 1$, which greatly simplifies computations.[17,27,35]

The matrix element of the radial interaction can be presented as a sum of three terms:

$$\hat{V}^R_{n_R\lambda_R n'_R\lambda'_R}=\delta_{\lambda_R,\lambda'_R}\frac{1}{2\mu_f}\Bigg(2\langle n_R\lambda_R|\frac{d}{dR}|n'_R\lambda'_R\rangle\frac{d}{dR}$$
$$+\langle n_R\lambda_R|\frac{d^2}{dR^2}|n'_R\lambda'_R\rangle$$
$$-\frac{1}{R^2}\langle n_R\lambda_R|j^2_{x'}+j^2_{y'}|n'_R\lambda'_R\rangle\Bigg), \quad (22)$$

where $j_{x'}$ and $j_{y'}$ are the body frame components of the electronic angular momentum.

As seen from Eq. (22), the radial interaction matrix elements are diagonal over the indices λ_R, λ'_R and do not depend on the total parity μ. Therefore, the set of closed-coupled scattering equations in Eq. (21) in the absence of the Coriolis interactions does not *explicitly* depend on the parity index μ and has the same form as the set of scattering equations for parity-unadapted radial wave functions $\chi^J_{n_R\Omega_R;n_k\Omega_k}(R)$, see Refs. 17 and 26. However, if $\lambda_R=0$ states involved in the photodissociation, this set of equations *implicitly* depends on the value of the parity index because of the condition in Eq. (8). The condition in Eq. (8) implies that for fixed values of μ and J, the set of equations in Eq. (21) contains either only Σ^+ or Σ^- interacting molecular states.

The matrix elements of the Coriolis interaction can be presented as

$$\hat{V}^C_{n_R\lambda_R;n'_R\lambda'_R}=\frac{2t_{\lambda_R}t_{\lambda'_R}}{\mu_f R^2}(\delta_{\lambda_R+1,\lambda'_R}\sqrt{(J-\lambda_R)(J+\lambda_R+1)}$$
$$\times\langle n_R\lambda_R|\hat{j}_{x'}|n'_R\lambda'_R\rangle$$
$$+\delta_{\lambda_R-1,\lambda'_R}\sqrt{(J+\lambda_R)(J-\lambda_R+1)}$$
$$\times\langle n_R\lambda_R|\hat{j}_{x'}|n'_R\lambda'_R\rangle$$
$$+\mu(-1)^{J-\varphi_R}\delta_{1-\lambda_R,\lambda'_R}\sqrt{(J+\lambda_R)(J-\lambda_R+1)}$$
$$\times\langle n_R-\lambda_R|\hat{j}_{x'}|n'_R\lambda'_R\rangle). \quad (23)$$

If $\lambda_R>1$, the third term in Eq. (23) is equal to zero because $\lambda'_R\geqslant 0$ and the Coriolis interaction matrix elements obey the selection rules $\lambda'_R=\lambda_R\pm 1$. In this case the matrix element does not depend on μ. If $\lambda_R=1$, all three terms in Eq. (23) can differ from zero and the Coriolis interaction matrix elements obey the selection rules $\lambda_R=1$, $\lambda'_R=0$ or $\lambda_R=1$, $\lambda'_R=2$. In this case, the matrix element in Eq. (23) implicitly depends on the parity index due to the condition $\mu=(-1)^{J+\varphi'_R+1}$ which implies that for fixed values of μ and J, only either Σ^+, or Σ^- states can contribute. If $\lambda_R=\frac{1}{2}$, the second term in Eq. (23) is equal to zero and the Coriolis interaction matrix elements obey the selection rules $\lambda_R=\frac{1}{2}$, $\lambda'_R=\frac{1}{2}$ or $\lambda_R=\frac{1}{2}$, $\lambda'_R=\frac{3}{2}$. In this case, the matrix element in Eq. (23) explicitly depends on the parity index μ. Finally, if $\lambda_R=0$, the second term in Eq. (23) is equal to zero and the Coriolis interaction matrix elements obey the selection rules $\lambda_R=0$, $\lambda'_R=1$. In this case, the matrix element implicitly depend on μ due to the condition $\mu=(-1)^{J-\varphi_R}$.

Therefore, in all cases, the set of closed-coupled equations in Eq. (21) in general either explicitly or implicitly depends on the parity index μ. The equations in Eq. (21) with the boundary conditions in Eq. (15) and (16) provide a link between the results of this paper and the formal scattering theory.

D. General expression for the photodissociation polarization cross section

We assume that the initial state of the parent molecule is bound and linear. The corresponding full molecular wave function $\Psi_{J_iM_i}$ in the dipole matrix elements in the photodissociation cross section in Eq. (3) in the parity-adapted $(J_in_i\lambda_i\mu_i)$ representation can be written in the form

$$\Psi_{J_iM_i} = t_{\lambda_i}\sqrt{\frac{2J_i+1}{4\pi}}\big(D^{J_i*}_{M_i\lambda_i}(\hat{\mathbf{R}},0)|n_i\lambda_i\rangle + \mu_i(-1)^{J_i-\varphi_i}D^{J_i*}_{M_i-\lambda_i}(\hat{\mathbf{R}},0)|n_i-\lambda_i\rangle\big)\chi_i(R), \qquad (24)$$

where J_i, M_i, $\lambda_i=|\Omega_i|$, n_i, and μ_i are quantum numbers describing the molecular initial state, $|n_i\lambda_i\rangle \equiv \Psi_{n_i\lambda_i}(R,\mathbf{r}_i)$ is an adiabatic body frame electronic initial state wave function, $\chi_i(R)$ is a radial (vibrational) wave function, and t_{λ_i} is a normalization factor defined in the same way as in Eq. (6).

The phase $(-1)^{\varphi_i}$ is defined by the behavior of the initial state electronic wave function $|n_i\lambda_i\rangle$ under reflection in the molecular xz plane, see Eq. (9). The initial state full wave function in Eq. (24) obeys the parity symmetry $\mu_i=\pm 1$ under inversion of all nuclear and electronic coordinates in the origin. If $\lambda_i=0$, the parity index μ_i is fixed by the relationship $\mu_i=(-1)^{J_i-\varphi_i}$ as shown in Eq. (8).

The dipole matrix elements in the photodissociation cross section in Eq. (3) can be evaluated by using the initial state wave function $\Psi_{J_iM_i}$ in Eq. (24) and the dissociative wave functions $\Psi^{-(\hat{\mathbf{k}},j,m)}(\mathbf{R},\mathbf{r}_i,E)$ in Eq. (13). After substituting Eqs. (13) and (24) into Eq. (3), integrating over the nuclear coordinates θ_R and ϕ_R, and producing angular momentum algebra transformations described in Appendix C, the expression for the photofragmentation cross section in Eq. (3) can be presented in the following form:

$$\begin{aligned}\sigma^{(j_A)}_{KQ}(\theta,\phi) = {} & C\frac{(2K+1)^{1/2}}{(2j_A+1)^{1/2}}\sum_{\mu,\mu_i}\sum_{J,J'}\sum_{\lambda_k,\lambda_k'}\sum_{\Omega_A,\Omega_A'}\sum_{j_B,\Omega_B}\sum_{n_k,n_k'}\sum_{k_d,q_d,q_k} t_{\lambda_k'}t_{\lambda_k}e^{i(\pi/2)(J-J')}\big(\mathcal{T}^{n_k'\lambda_k'}_{j_A\Omega_A'j_B\Omega_B} + \mu(-1)^{J'-\phi_{k'}}\mathcal{T}^{n_k'-\lambda_k'}_{j_A\Omega_A'j_B\Omega_B}\big)\\ & \times\big(\mathcal{T}^{n_k\lambda_k}_{j_A\Omega_Aj_B\Omega_B} + \mu(-1)^{J-\phi_k}\mathcal{T}^{n_k-\lambda_k}_{j_A\Omega_Aj_B\Omega_B}\big)^*(-1)^{q_k}E_{k_dq_d}(\mathbf{e})D^{K*}_{Qq_k}(\theta,\phi,0)D^{k_d}_{q_dq_k}(\theta,\phi,0)C^{j_A\Omega_A'}_{j_A\Omega_AK-q_k}C^{J\Omega_k}_{J'\Omega_k'k_dq_k}\\ & \times(-1)^{J+J_i}[(2k_d+1)(2J'+1)]^{1/2}\begin{Bmatrix} J' & J & k_d\\ 1 & 1 & J_i\end{Bmatrix}\sum_{\lambda_R,\lambda_R'}\sum_{q,q'}\sum_{n_R,n_R'}\sum_{J_i,\lambda_i} t_{\lambda_R'}t_{\lambda_R}C^{J'\lambda_R'}_{J_i(\lambda_R'-q')1q'}C^{J\lambda_R}_{J_i(\lambda_R-q)1q}(1-\mu_i\mu)\\ & \times\langle R^{-1}\chi^{J'\mu}_{n_R'\lambda_R'n_k'\lambda_k'}(R)\Psi_{n_R'\lambda_R'}(R,\mathbf{r}_i)|\hat{d}_{q'}|\chi_i(R)\Psi_{\mu_i\lambda_i}(R,\mathbf{r}_i)\rangle\langle R^{-1}\chi^{J\mu}_{n_R\lambda_Rn_k\lambda_k}(R)\Psi_{n_R\lambda_R}(R,\mathbf{r}_i)|\hat{d}_q|\chi_i(R)\Psi_{\mu_i\lambda_i}(R,\mathbf{r}_i)\rangle^*, \qquad (25)\end{aligned}$$

where $\Omega_k=\Omega_A+\Omega_B$, $\Omega_k'=\Omega_A'+\Omega_B$, the subscript indices i, R, and k relate to the initial, intermediate, and outgoing (final) states, respectively, and the term $(1-\mu_i\mu)$ is nonzero only for $\mu_i=-\mu$, in agreement with the known dipole transition selection rule.[42]

Here summation over the indices J, J', λ_i, λ_R, λ_R', λ_k, and λ_k' is proceeded over all possible positive half-integer numbers or over all possible non-negative integer numbers, including zero. Summation over the indices Ω_A, Ω_A', and Ω_B is proceeded over all possible positive and negative half-integer or integer numbers. Summation over the indices q and q' is proceeded over the values q, $q'=0,\pm 1$.[8] The value of the fragment A total angular momentum j_A is assumed to be fixed.

The transition dipole matrix elements in the last line of Eq. (25) describe excitation of the parent molecule from the initial state $|i\rangle$ to the intermediate state $|R\rangle$ and the following molecular dynamics to the final state $|k\rangle$. The initial state electronic wave function $\Psi_{\mu_i\lambda_i}$ is given by

$$\Psi_{\mu_i\lambda_i} = t_{\lambda_i}[\Psi_{n_i\lambda_i}(R,\mathbf{r}_i) + \mu_i(-1)^{J_i-\phi_i}\Psi_{n_i-\lambda_i}(R,\mathbf{r}_i)]. \qquad (26)$$

As can be shown by using Eq. (26), due to the axial symmetry of the molecule, the transition matrix elements in Eq. (25) obey the selection rule $\lambda_R=|\lambda_i\pm q|$, which is equivalent to the known selection rule $\Omega_R=\Omega_i+q$ used in the theory where the quantum numbers Ω_R and Ω_i can take either positive or negative values.[5]

The term $E_{k_dq_d}(\mathbf{e})$ in Eq. (25) is the light polarization matrix:[29]

$$E_{k_dq_d}(\mathbf{e}) = [\mathbf{e}\otimes\mathbf{e}^*]_{k_dq_d} = \sum_{pp'}(-1)^pC^{k_dq_d}_{1-p'1p}e_{-p'}(e_{-p})^*, \qquad (27)$$

where the rank of the polarized light k_d is limited to the values $k_d=0,1,2$.

In the practically important cases of fully linearly or circularly polarized light, this matrix can be presented in the following simple form:[43]

$$E_{k_dq_d} = (-1)^{p+k_d}C^{k_d0}_{1p1-p}\mathrm{C}_{k_dq_d}(\mathbf{n}), \qquad (28)$$

where the index p is equal to 0 in the case of linear polarization and to ± 1 in the case of right/left circular polarization, respectively; $C_{KQ}(\mathbf{n})=[4\pi/(2K+1)]^{1/2}Y_{KQ}(\mathbf{n})$ is a modified spherical harmonic[44] and $\mathbf{n}$ is the direction of light polarization in the case of linear polarized light and the direction of light propagation in the case of circularly polarized light. Explicit expressions for the matrix $E_{k_dq_d}$ as a function of the coordinates of the vector $\mathbf{n}$ can be found in Ref. 39. Note that the polarization matrix Φ_{kq} used in Ref. 39 is related to the polarization matrix E_{kq} as $\Phi_{kq}=(-1)^{k+1}E_{kq}$.

Summation over the total parity of the initial and excited states is proceeded in Eq. (25) over μ, $\mu_i=\pm 1$, however, due to the selection rule $\mu=-\mu_i$ this double summation is equivalent to the summation over the μ_i only. At a certain value of the total angular momentum J_i, the value of μ_i is fixed for $\lambda_i=0$ states according to condition (8), however, if $\lambda_i\neq 0$, summation over $\mu_i=\pm 1$ is proceeded according to Eqs. (25) and (26). Note that summation over λ, λ', and μ in the parity-adapted representation is used instead of summation over Ω and Ω' in the representation where the parity is not incorporated, see Appendix A.

The polarization cross section in Eq. (25) is still a fully quantum-mechanical result which explicitly incorporates the total parity of the molecular wave function. Relying only on the assumption of the electric dipole transition it can, in principle, be used for fast as well slow dissociation processes. The expression in Eq. (25) must be equivalent to the dissociation cross section recently reported by Kuznetsov and Vasyutinskii in Eq. (9) in Ref. 26, where the total parity was not incorporated.[45] The *angular* (kinematic) parts in these two expressions are the same; however, the *dynamical* parts are different. The advantage of the expression in Eq. (25) is that under the "proper" molecular wave function basis, the set of closed-coupled equations in Eq. (21) is separated into two independent blocks corresponding to the total parity values $\mu=1$ and $\mu=-1$.

The indices $q_k=\Omega_k-\Omega_k'=\Omega_A-\Omega_A'$ in the polarization cross section in Eq. (25) are limited to the values $q_k=0,\pm 1,\pm 2$. The terms with $q_k=0$ describe incoherent excitation of the outgoing dissociation channels ($\lambda_k=\lambda_k'$), while the terms with $q_k\neq 0$ describe possible interference between these states ($\lambda_k=|\lambda_k'\pm 1|,|\lambda_k'\pm 2|$).

In general, the expression for the polarization cross section in Eq. (25) is rather complicated and does not allow simple experimental data development and interpretation. Great simplification can be achieved by formation of the J-independent dynamical terms and isolating them from the kinematical terms which can be done by using certain approximations.

The axial recoil approximation which assumes the rectilinear photofragment trajectory has been used by many other authors, see e.g., Refs. 5, 8, 9, and 19–25. Within this approximation, the scattering wave function $\chi^J(R)$ weakly depends on J. Having in mind that J and J' are limited to the values J, $J'=J_i,J_i\pm 1$, the transition dipole matrix elements can be calculated at $J=J'=J_i$. Then, after summation over all possible values of the total angular momentum, J, J', the obtained polarization cross section describes the limit of instant photodissociation.

The quasiclassical approximation in the case of direct photodissociation and the approximation of the slow predissociation are discussed in the next two sections.

In the following, it will be convenient to transform in Eq. (25) from the un-normalized excitation cross section $\sigma^{(j_A)}_{KQ}(\theta,\phi)$ to the normalized atomic state multipoles $\rho^{(j_A)}_{KQ}(\theta,\phi)$ using the expression[8]

$$\rho^{(j_A)}_{KQ}(\theta,\phi)=\frac{\sigma^{(j_A)}_{KQ}(\theta,\phi)}{(2j_A+1)^{1/2}\sigma_0}, \tag{29}$$

where σ_0 is the normalization factor which is equal to the zeroth-order photodissociation cross section averaged over all recoil directions θ, ϕ: $\sigma_0=\langle\sigma^{(j_A)}_{00}(\theta,\phi)\rangle$.

III. DIRECT PHOTODISSOCIATION

A. Polarization cross section

The expressions overcoming the axial recoil approximation have been recently reported by Kuznetsov and Vasyutinskii[26] who used the quasiclassical approximation and the high-J limit, $J, J', J_i \gg 1$. The quasiclassical approximation allows to separate the regions of the internuclear distance R where the dissociation dynamics is mostly adiabatic from the relatively narrow regions where the nonadiabatic interactions occur.[17] Within this approximation, the radial wave function $\chi^J_{n_R\lambda_R;n_k\lambda_k}$ in Eq. (16) can be factorized as

$$\chi^J_{n_R\lambda_R;n_k\lambda_k}\approx \exp(-i\delta^J_{n_k\lambda_k})\tilde{\chi}^J_{n_R\lambda_R;n_k\lambda_k}, \tag{30}$$

where the exponent $\exp(-\delta^J_{n_k\lambda_k})$ rapidly oscillates as a function of J, while the term $\tilde{\chi}^J_{n_R\lambda_R;n_k\lambda_k}$ weakly depends on J in the region $J_i\pm 1$. The phase $\delta^J_{n_k\lambda_k}$ is equivalent to the elastic scattering phase in the formal scattering theory.

Within the quasiclassical approximation the radial scattering wave functions $\chi^J_{n_R\lambda_R;n_k\lambda_k}$ in Eq. (16) are presented in the form shown in Eq. (30). In the high-J limit, the phase is related to the classical angle of rotation of the molecular axis during dissociation γ as

$$\delta^{J'}_{n_k'\lambda_k'}-\delta^J_{n_k\lambda_k}\approx\left(\frac{\pi}{2}-\gamma\right)(J'-J), \tag{31}$$

where we assumed that the angle γ does not depend on J within the range $J_i-1\leqslant J\leqslant J_i+1$ and on n_k, n_k'.

The case $\gamma=0$ corresponds to the axial recoil approximation. If $\gamma\neq 0$, the phase factors $\delta^J_{n_k\lambda_k}$ can be factored out from the dipole moment matrix elements in Eq. (25) and summation over the total angular momentum values J and J' can be proceeded in the way, similar to that used by Kuznetsov and Vasyutinskii.[26] The details of the calculation are given in Appendix D. By using Eq. (29), the obtained result can be presented in the following form:

$$\begin{aligned}\rho^{(j_A)}_{KQ}(\theta,\phi)=&\frac{3}{4\pi}\frac{(2K+1)^{1/2}}{(2j_A+1)^{1/2}}\sum_{k_d,q_d}\sum_{q,q'}\sum_{Q',q_k}\\&\times(-1)^{k_d+q+q_k}\sqrt{2k_d+1}\\&\times E_{k_dq_d}(\mathbf{e})D^{K*}_{Qq_k}(\phi,\theta,0)D^{k_d}_{q_dq_k}(\phi,\theta,0)\\&\times D^{k_d}_{q_kQ'}\left(\frac{\pi}{2},\gamma,-\frac{\pi}{2}\right)\\&\times\begin{pmatrix}1 & 1 & k_d\\ q' & -q & Q'\end{pmatrix}\mathcal{N}^{-1}\sum_{\tilde{q},\tilde{q}'}f_K(q,q',\tilde{q},\tilde{q}')\\&\times\delta_{(\tilde{q}-\tilde{q}'),q_k}.\end{aligned} \tag{32}$$

The generalized dynamical function $f_K(q,q',\tilde{q},\tilde{q}')$ in Eq. (32) can be written as

$$f_K(q,q',\tilde{q},\tilde{q}') = \sum_s (-1)^{2J_i+K+j_A+\Omega_A'} \times \begin{pmatrix} j_A & j_A & K \\ -\Omega_A & \Omega_A' & (\tilde{q}-\tilde{q}') \end{pmatrix} \times \langle \Psi_{\text{ex}}' | \hat{d}_{q'} | \chi_i(R) \Psi_i \rangle \langle \Psi_{\text{ex}} | \hat{d}_q | \chi_i(R) \Psi_i \rangle^*, \tag{33}$$

where the excited state wave function Ψ_{ex} is given by

$$\begin{aligned} \Psi_{\text{ex}} = \frac{4}{R} \sum_{\lambda_R,\lambda_k} t_{\lambda_k}^2 t_{\lambda_R}^2 [(& \mathcal{T}_{j_A\Omega_A j_B\Omega_B}^{n_k\lambda_k} \tilde{\chi}_{n_R\lambda_R,n_k\lambda_k}^{J_i}(R) \\ & + \mathcal{T}_{j_A\Omega_A j_B\Omega_B}^{n_k-\lambda_k} \tilde{\chi}_{n_R\lambda_R,n_k-\lambda_k}^{J_i}(R)) | n_R\lambda_R \rangle \\ & + (\mathcal{T}_{j_A\Omega_A j_B\Omega_B}^{n_k\lambda_k} \tilde{\chi}_{n_R-\lambda_R,n_k\lambda_k}^{J_i}(R) \\ & + \mathcal{T}_{j_A\Omega_A j_B\Omega_B}^{n_k-\lambda_k} \tilde{\chi}_{n_R-\lambda_R,n_k-\lambda_k}^{J_i}(R)) | n_R-\lambda_R \rangle] \\ \equiv \frac{1}{R} \sum_{\Omega_R,\Omega_k} & \mathcal{T}_{j_A\Omega_A j_B\Omega_B}^{n_k\Omega_k} \tilde{\chi}_{n_R\Omega_R,n_k\Omega_k}^{J_i}(R) | n_R\Omega_R \rangle . \end{aligned} \tag{34}$$

The product of two initial state wave functions $|\Psi_i\rangle\langle\Psi_i|$ in Eq. (33) can be presented as

$$\begin{aligned} |\Psi_i\rangle\langle\Psi_i| &= \sum_{\mu_i,\lambda_i} |\chi_{\lambda_i}(R)\Psi_{\mu_i\lambda_i}\rangle\langle\chi_{\lambda_i}(R')\Psi_{\mu_i\lambda_i}| \\ &= \sum_{\mu_i,\lambda_i} t_{\lambda_i}^2 \chi_{\lambda_i}(R)\chi_{\lambda_i}^*(R')[|\Psi_{n_i\lambda_i}(R,\mathbf{r}_i)\rangle \\ &\quad + \mu_i(-1)^{J_i-\phi_i}|\Psi_{n_i-\lambda_i}(R,\mathbf{r}_i)\rangle][\langle\Psi_{n_i\lambda_i}(R',\mathbf{r}_i)| \\ &\quad + \mu_i(-1)^{J_i-\phi_i}\langle\Psi_{n_i-\lambda_i}(R',\mathbf{r}_i)|] \\ &\equiv \sum_{\Omega_i} |\chi_{\Omega_i}(R)\Psi_{n_i\Omega_i}(R,\mathbf{r}_i)\rangle\langle\chi_{\Omega_i}(R')\Psi_{n_i\Omega_i}(R',\mathbf{r}_i)| . \end{aligned} \tag{35}$$

The initial state electronic wave function $\Psi_{\mu_i\lambda_i}$ is defined in Eq. (26). The summation index s in Eq. (33) is an aggregate of the indices n_B, j_B, Ω_B, Ω_A, Ω_A', n_R, n_R', n_k, n_k'.

The index q_k is equal to $q_k=\Omega_A-\Omega_A'=\tilde{q}-\tilde{q}'$ and describes the interference between the outgoing channels $\Omega_k=\Omega_A+\Omega_B$ and $\Omega_k'=\Omega_A'+\Omega_B$, while the index Q' is equal to $Q'=q-q'$ and describes the interference between the intermediate channels λ_R and λ_R'. The indices Q' and q_k are equal to each other in the case of radial nonadiabatic transitions, while in the case of the Coriolis transitions, these indices can be either the same or different from each other. The Wigner *D* functions

$$D_{q_kQ'}^{k_d}(\pi/2,\gamma,-\pi/2) = \exp[i(\pi/2)(Q'-q_k)]d_{q_kQ'}^{k_d}(\gamma)$$

in Eq. (32) are the *rotation factors* which were introduced in Ref. 26. They depend on the classical angle of rotation of the molecular axis during dissociation γ and describe the influence of the molecular axis rotation on the photofragment angular momentum polarization. The values of the d functions $d_{q_kQ'}^k(\gamma)$ of the rank $k=0,1,2$ and all possible projections Q' and q_k as function of the angle γ are tabulated in Ref. 44. In the case $\gamma=0$, the indices q_k and Q' are equal to each other due to the d-function symmetry. In this limit, the contribution of the Coriolis interaction to the polarization cross section can be neglected.[17]

The important feature of Eqs. (32)–(34) is that they *do not* contain the parity index μ_R. Moreover, using Eq. (35), it can be shown that Eqs. (32)–(34) are *exactly equivalent* with Eq. (18) in Ref. 26 which was obtained without incorporating the molecular total parity. Therefore, the parity-adapted and parity-unadapted formalisms result in the same expressions for the photofragment state multipoles in the case of the fast photodissociation. The obtained result can be treated as a formal proof of validity of the parity-unadapted formalism which was used in practically all theoretical papers on the photofragment orientation and alignment published elsewhere.[8,9,19,21–26]

The indices $\tilde{q}$, $\tilde{q}'$ in Eq. (33) are defined as $\tilde{q}=\Omega_k-\Omega_i$, $\tilde{q}'=\Omega_k'-\Omega_i$. In general, Eqs. (32) and (33) take into consideration radial (homogeneous) and Coriolis nonadiabatic transitions as well as molecular axis rotation. The index difference $\tilde{q}-q=\Omega_k-\Omega_R$ has clear physical meaning: it is equal to the change in the projection of the molecular electronic angular momentum due to the Coriolis interactions. Particularly, the radial nonadiabatic transitions in the absence of the Coriolis interactions result in the relations $\tilde{q}-q=0$, $\tilde{q}'-q'=0$; however, the Coriolis nonadiabatic transitions can result in the relations $\tilde{q}-q\neq 0$, $\tilde{q}'-q'\neq 0$. In the first-order approximation of the Coriolis interaction, the corresponding matrix element in Eq. (23) obeys the selection rules $\tilde{q}-q=\pm 1$, while r several successive Coriolis interactions in the molecule (r-order approximation) can result in the selection rules $\tilde{q}-q=\pm r$, where $|r|>1$. In the following, we restrict ourselves to the first-order Coriolis interactions which fulfill the selection rules $\tilde{q}=q\pm 1$ and/or $\tilde{q}'=q'\pm 1$ neglecting the higher-order Coriolis interactions.

The value $\mathcal{N}$ in Eq. (32) is a normalization factor:

$$\mathcal{N} = f_0(0,0,0,0) + 2f_0(1,1,1,1) + 2f_0(0,0,1,1) + 2f_0(1,1,0,0) + 2f_0(1,1,2,2), \tag{36}$$

where the first line describes possible radial nonadiabatic transitions, while the second line describes three dissociation mechanisms due to the first-order approximation of the Coriolis nonadiabatic interaction.

Using Eq. (33), one can show that the dynamical functions $f_K(q,q',\tilde{q},\tilde{q}')$ obey the following symmetry rules:

$$f_K(-q,-q',-\tilde{q},-\tilde{q}') = (-1)^K f_K(q,q',\tilde{q},\tilde{q}')$$

$$f_K(q',q,\tilde{q}',\tilde{q}) = (-1)^{\tilde{q}-\tilde{q}'} f_K^*(q,q',\tilde{q},\tilde{q}') .$$

Using the symmetry properties of the Wigner D functions,[44] the polarization cross section in Eq. (32) can be transformed to a more symmetric form which is convenient for the analysis of the role of the Coriolis interactions:

$$\rho_{KQ}^{(j_A)}(\theta,\phi) = -\frac{\sqrt{3}}{4\pi(2j_A+1)^{1/2}}\sum_{N,k_d}(2N+1) \times [C_N(\theta,\phi)\otimes E_{k_d}(\mathbf{e})]_{KQ}P_{Nk_d}^{K}, \tag{37}$$

where the term in square brackets is the irreducible tensor product:[44]

$$[C_N(\theta,\phi)\otimes E_{k_d}(\mathbf{e})]_{KQ} = \sum_{\zeta,q_d} C_{N\zeta k_d q_d}^{KQ} C_{N\zeta}(\theta,\phi)E_{k_d q_d}(\mathbf{e}) \tag{38}$$

of the modified spherical harmonics $C_{N\zeta}(\theta,\phi)$ and the light polarization matrix $E_{k_d q_d}(\mathbf{e})$.

The term $P_{Nk_d}^{K}$ in Eq. (37) is the linestrength factor which depends only on the photofragment rank K, light polarization rank k_q, and the spatial spherical harmonic rank N. Using the symmetry properties of the dynamical functions in Eq. (37), the linestrength factor $P_{Nk_d}^{K}$ can be presented in the form

$$P_{Nk_d}^{K} = -\sum_{q,q',q_k}\sqrt{3(2k_d+1)}\begin{pmatrix} N & k_d & K \\ 0 & |q_k| & -|q_k| \end{pmatrix} \times(-1)^q D_{|q_k|Q'}^{k_d}\left(\frac{\pi}{2},\gamma,-\frac{\pi}{2}\right) \times\begin{pmatrix} 1 & 1 & k_d \\ q' & -q & Q' \end{pmatrix}\mathcal{N}^{-1}\sum_{\tilde{q},\tilde{q}'} f_K(q,q',\tilde{q},\tilde{q}')\,\delta_{\tilde{q}-\tilde{q}',|q_k|}, \tag{39}$$

where $|q_k|$ is the modulus of the index q_k which is limited to the values $|q_k|=0,1,2$ and the spatial spherical harmonic rank N is limited to even integer values from the interval $0,\ldots,(K+k_d)$.

B. Analysis of general expressions for the anisotropy parameters: The role of the Coriolis interaction

The generalized dynamical functions $f_K(q,q',\tilde{q},\tilde{q}')$ in Eqs. (32) and (39) contain all information on the photodissociation dynamics including probabilities of the radial (homogeneous) and Coriolis nonadiabatic transitions and the phase difference between different dissociation channels. As mentioned above, if the Coriolis nonadiabatic interactions can be neglected, the indices $q,q',\tilde{q},\tilde{q}'$ fulfill the relationships $\tilde{q}=q$ and $\tilde{q}'=q'$, and the generalized dynamical functions $f_K(q,q',q,q')$ become equivalent to the dynamical functions $f_K(q,q')$ introduced elsewhere.[5,21] For this case, the angle-recoil distributions of the photofragment state multipoles have been tabulated in terms of the *anisotropy parameters* β, α_K, γ_K, γ'_K, η_K, and s_K of the rank $K=1,2$ by Picheyev *et al.*[32] and by Bracker *et al.*[8] (see also the review paper in Ref. 13). The distributions of the high-rank state multipoles, $K=3,4$, have been tabulated by Smolin *et al.*[33,34] The anisotropy parameters have been defined in Refs. 8 and 32–34 as linear combinations of the normalized dynamical functions $f_K(q,q')$ of the same rank.

As will be shown later, the photofragment angle-recoil distributions in Eqs. (32) and (39) can still be expressed in terms of the anisotropy parameters[8,13,32–34] which can be expressed as linear combinations of the generalized dynamical functions $f_K(q,q',\tilde{q},\tilde{q}')$. In the case if the Coriolis nonadiabatic transitions are important, the dynamical functions of the rank K which contribute to the same anisotropy parameter in general cannot be isolated from each other from experimental data without additional theoretical analysis.

Note that the body frame *polarization parameters* $\mathbf{a}_K^{(q)}(\parallel,\perp)$ introduced by Rakitzis *et al.*[19,20] are defined for the case of the fast photodissociation in the absence of the Coriolis nonadiabatic interactions and therefore can be used for the analysis of only this type of the photochemical reactions.

We now consider the photolysis of a linear molecule taking into account both radial and Coriolis nonadiabatic interactions and present explicit expressions for the anisotropy parameters of the rank $K=0$, 1, and 2 as a function of the corresponding dynamical functions $f_K(q,q',\tilde{q},\tilde{q}')$. It will be shown that in general each of the anisotropy parameter of a certain rank can be presented as sum of several dynamical functions describing a particular dissociation mechanism each.

1. *K*=0

In the case $K=0$, $Q=0$, the state multipole $\rho_{00}^{(j_A)}(\theta,\phi)$ in Eq. (37) describes the angular distribution of the photofragments. If the light is linearly polarized, Eq. (37) can be presented in the standard form[1]

$$\rho_{00}^{(j_A)}(\Theta) = \frac{1}{4\pi(2j_A+1)^{1/2}}[1+\beta P_2(\cos\Theta)], \tag{40}$$

where β is the anisotropy parameter and $P_2(\cos\Theta)$ is the Legendre polynomial of the second order, where Θ is the angle between the light polarization axis $\mathbf{e}$ and the recoil direction.

In the first-order approximation over the Coriolis interaction, the parameter β in Eq. (40) is given by

$$\beta = 2d_{00}^{2}(\gamma)\frac{[f_0(0,0,0,0)-f_0(1,1,1,1)]}{\mathcal{N}} + 2d_{00}^{2}(\gamma)\frac{[2f_0(0,0,1,1)-f_0(1,1,0,0)-f_0(1,1,2,2)]}{\mathcal{N}} - 4\sqrt{3}d_{01}^{2}(\gamma)\frac{\mathrm{Im}[f_0(1,0,1,1)+f_0(1,0,0,0)]}{\mathcal{N}} + 2\sqrt{6}d_{02}^{2}(\gamma)\frac{f_0(1,-1,0,0)}{\mathcal{N}}, \tag{41}$$

where the four terms in the right-hand side describe contributions to the parameter β from different dissociation mechanisms.

The index $q_k=\Omega_k-\Omega'_k$ in all of the terms in Eq. (41) is equal to zero, indicating that no coherence occurs in the final molecular state.

The first term in Eq. (41) consists of two parts in the square brackets which describe incoherent optical parallel and perpendicular excitation of the parent molecule followed by the radial nonadiabatic transitions. The same term describes the photodissociation in the absence of nonadiabatic interactions. The examples of this photodissociation mecha-

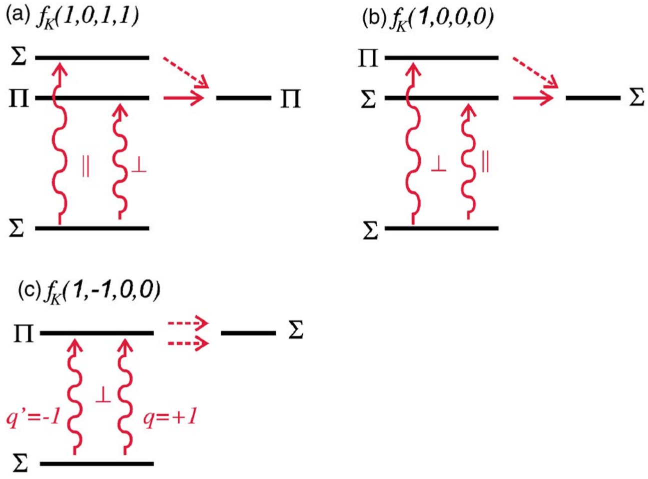

FIG. 2. (Color online) [(a)–(c)] Examples of dissociation mechanisms resulting in single final states via coherent optical excitation of the parent molecule. The notations are the same as in Fig. 1. These mechanisms can contribute to the anisotropy parameters β, α_K, and s_K.

nism are $\Sigma\rightarrow\Sigma\rightarrow\Sigma$ and $\Sigma\rightarrow\Pi\rightarrow\Pi$, where the first symbol denotes the initial state of the parent molecule and two other symbols denote excited states. These dissociation mechanisms are shown schematically in Figs. 1(a) and 1(b). The dynamical factors $f_0(0,0,0,0)$ and $f_0(1,1,1,1)$ are always real. The contribution from this term is equivalent to the known expression for the parameter β in the absence of the Coriolis interactions.[5,8,13]

All other terms in Eq. (41) can contribute to the β value only if the Coriolis interaction contributes to the dissociation dynamics. The term in the second line in Eq. (41), where all three dynamical factors $f_0(0,0,1,1)$, $f_0(1,1,0,0)$, and $f_0(1,1,2,2)$ are real consists of three parts in the square brackets which describe parallel or perpendicular incoherent optical excitation of the parent molecule followed by the Coriolis nonadiabatic transitions. The examples of the photolysis through this mechanism are $\Sigma\rightarrow\Sigma\rightarrow\Pi$, $\Sigma\rightarrow\Pi\rightarrow\Sigma$, and $\Sigma\rightarrow\Pi\rightarrow\Delta$, which are schematically shown in Figs. 1(c)–1(e), respectively.

The term in the third line in Eq. (41) consists of two parts in the square brackets which describe coherent optical excitation of a perpendicular and a parallel transition to the superposition of intermediate states Ω_R and Ω_R' followed by a Coriolis nonadiabatic transitions to the incoherent final state Ω_k. Both dynamical factors $f_0(1,0,0,0)$ and $f_0(1,0,1,1)$ can be in general complex. Examples of this mechanism, $\Sigma\rightarrow(\Sigma,\Pi)\rightarrow\Pi$ and $\Sigma\rightarrow(\Sigma,\Pi)\rightarrow\Sigma$, are shown in Figs. 2(a) and 2(b).

The term in the fourth line in Eq. (41) describes coherent optical excitation of two perpendicular transitions to the intermediate states Ω_R and Ω_R' followed by the Coriolis nonadiabatic transitions from both intermediate states to a single final state Ω_k. An example of the photodissociation through this mechanism, $\Sigma\rightarrow(\Pi,\Pi)\rightarrow\Sigma$, is shown in Fig. 2(c). The dynamical factor $f_0(1,-1,0,0)$ is always real.

The dependence on the angle of rotation of the recoil axis γ for the two latest terms is given by the d functions $d^2_{01}(\gamma)$ and $d^2_{02}(\gamma)$. Both of them are equal to zero in the axial recoil approximation ($\gamma=0$).[45]

All dissociation mechanisms considered in Eq. (41) result in the same recoil photofragments angular distribution in Eq. (40) and therefore they cannot be directly separated from experimental data containing only one anisotropy parameter β without determination of the higher rank ($K>0$) anisotropy parameters and/or theoretical analysis.

2. $K=1$

The rank $K=1$ state multipoles describe photofragment orientation. As known,[13,32] in general, there are three independent anisotropy parameters of the first rank: α_1, γ_1, and γ_1' describing angular dependence of the photofragment orientation at any experimental geometry. Each of the parameter can be described by a unique angular distribution in the rank $K=1$ photofragment state multipoles which, however, depends on the experimental geometry. These angular distributions are tabulated in Refs. 13 and 32. The parameter γ_1' is usually detected in experiments with linear polarization of the photolysis light, while the parameters α_1 and γ_1 are usually detected in experiments with circular polarization of the photolysis light. The expressions for these anisotropy parameters in the case of the fast photodissociation of a linear molecule as a function of the dynamical functions $f_K(q,q',\tilde{q},\tilde{q}')$ in the first-order approximation of the Coriolis interaction are given below.

Parameter α_1

$$\begin{aligned}\alpha_1 &= d^1_{00}(\gamma)\frac{f_1(1,1,1,1)}{\mathcal{N}}\\ &\quad + d^1_{00}(\gamma)\left[\frac{f_1(1,1,0,0)}{\mathcal{N}}+\frac{f_1(1,1,2,2)}{\mathcal{N}}\right]\\ &\quad + 2d^1_{01}(\gamma)\frac{\mathrm{Im}[f_1(1,0,1,1)+f_1(1,0,0,0)]}{\mathcal{N}}. \qquad (42)\end{aligned}$$

Here, the index $q_k=\tilde{q}-\tilde{q}'$ in all terms is equal to zero, which indicates that no coherence is produced in the final state $|n_k,\Omega_k\rangle$.

The first term in Eq. (42) describes incoherent optical excitation of a perpendicular transition followed by radial nonadiabatic interaction or no nonadiabatic interaction at all. This term represents the known mechanism of producing the photofragment orientation with circularly polarized light in the absence of the Coriolis interactions which is described in detail elsewhere.[13,26,46,47] An example of this photodissociation mechanism, $\Sigma\rightarrow\Pi\rightarrow\Pi$, is shown in Fig. 1(b). The term in the second line of Eq. (42) consists of two parts in the square brackets and describes incoherent excitation of a perpendicular transition followed by the Coriolis nonadiabatic transitions to a single molecular state. Examples of this photodissociation mechanism, $\Sigma\rightarrow\Pi\rightarrow\Sigma$ and $\Sigma\rightarrow\Pi\rightarrow\Delta$, are shown in Figs. 1(d) and 1(e), respectively.

The term in the third line in Eq. (42) which consists of two terms in the square brackets describes coherent optical excitation of a perpendicular and a parallel transition followed by the Coriolis nonadiabatic transitions to a single molecular state. Examples of this mechanism, $\Sigma\rightarrow(\Pi,\Sigma)$

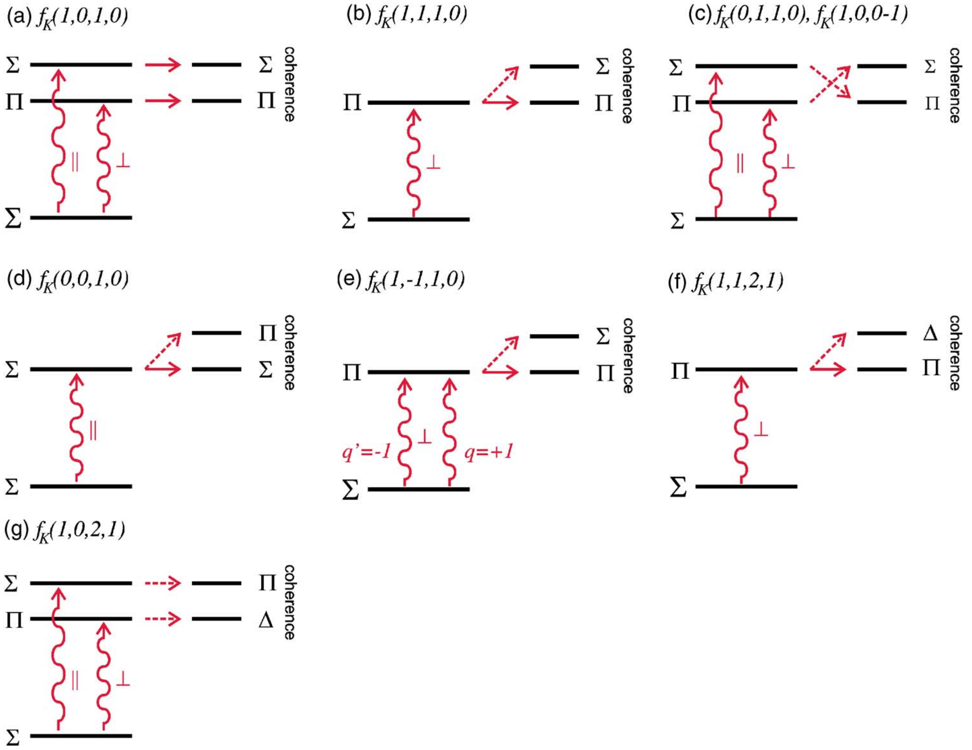

FIG. 3. (Color online) [(a)–(g)] Examples of dissociation mechanisms resulting in $\Delta\Omega=\pm 1$ coherent superposition of the final states. The notations are the same as in Fig. 1. These dissociation mechanisms can contribute to the anisotropy parameters γ_K and γ'_K of the rank $K\geq 1$.

$\rightarrow\Pi$ and $\Sigma\rightarrow(\Pi,\Sigma)\rightarrow\Sigma$, are shown in Figs. 2(a) and 2(b). This term vanishes in the axial recoil approximation because $d^1_{01}(\gamma)\sim\sin\gamma$.[44]

Parameter γ_1

$$\gamma_1 = 2d^1_{11}(\gamma)\frac{\mathrm{Re}[f_1(1,0,1,0)]}{\mathcal{N}} - 2d^1_{10}(\gamma)\left[\frac{\mathrm{Im}[f_1(1,1,1,0)]}{\mathcal{N}} + \frac{\mathrm{Im}[f_1(1,1,2,1)]}{\mathcal{N}}\right] + 2d^1_{1-1}(\gamma)\frac{\mathrm{Re}[f_1(0,1,1,0)]}{\mathcal{N}} + 2d^1_{11}(\gamma)\left[\frac{\mathrm{Re}[f_1(1,0,2,1)]}{\mathcal{N}} + \frac{\mathrm{Re}[f_1(1,0,0,-1)]}{\mathcal{N}}\right]. \tag{43}$$

Here, the difference $\tilde{q}-\tilde{q}'$ in all terms is equal to $q_k=1$, which indicates coherent superposition of the final states of different symmetry.

The first term in Eq. (43) describes coherent optical excitation of a perpendicular and a parallel transition followed by the radial nonadiabatic interaction or no nonadiabatic interaction at all. This term corresponds to the known coherent mechanism resulting in the production of the photofragment orientation with circularly polarized light in the absence of the Coriolis interactions.[13,26,47] An example of this mechanism, $\Sigma\rightarrow(\Pi,\Sigma)\rightarrow(\Pi,\Sigma)$, is shown in Fig. 3(a).

All other terms in Eq. (43) can differ from zero only in the presence of the Coriolis interaction. In particular, the second term in Eq. (43) which consists of two parts describes incoherent optical excitation of a perpendicular transition followed by a Coriolis transition. Examples of this mechanism, $\Sigma\rightarrow\Pi\rightarrow(\Pi,\Sigma)$ and $\Sigma\rightarrow\Pi\rightarrow(\Pi,\Delta)$, are shown in Figs. 3(b) and 3(f), respectively. The contribution from these terms are equal to zero in the axial recoil approximation because the corresponding rotational factor $d^1_{01}(\gamma)$ is equal to zero at $\gamma=0$.

All other terms in Eq. (43) describe coherent optical excitation of a perpendicular and a parallel transitions followed by Coriolis transitions. Examples of this mechanism, $\Sigma\rightarrow(\Pi,\Sigma)\rightarrow(\Sigma,\Pi)$ and $\Sigma\rightarrow(\Pi,\Sigma)\rightarrow(\Delta,\Pi)$, are shown in Figs. 3(c) and 3(g). Contribution from the former term is zero in the axial recoil approximation, while the remaining term can differ from zero in the axial recoil approximation because the corresponding rotational factor $d^1_{11}(\gamma)\sim(1+\cos\gamma)$ differs from zero at $\gamma=0$.

Parameter γ'_1

$$\gamma'_1 = 2d^2_{11}(\gamma)\frac{\mathrm{Im}[f_1(1,0,1,0)]}{\mathcal{N}} + \frac{2\sqrt{3}}{3}d^2_{10}(\gamma)\times\left[\frac{\mathrm{Re}[f_1(1,1,1,0)]}{\mathcal{N}} + \frac{\mathrm{Re}[f_1(1,1,2,1)]}{\mathcal{N}}\right] + 2d^2_{1-1}(\gamma)\frac{\mathrm{Im}[f_1(0,1,1,0)]}{\mathcal{N}} + 2d^2_{11}(\gamma)\times\left[\frac{\mathrm{Im}[f_1(1,0,2,1)]}{\mathcal{N}} + \frac{\mathrm{Im}[f_1(1,0,0,-1)]}{\mathcal{N}}\right] - 2\sqrt{2}d^2_{12}(\gamma)\frac{\mathrm{Re}[f_1(1,-1,1,0)]}{\mathcal{N}} - \frac{4\sqrt{3}}{3}d^2_{10}(\gamma)\frac{\mathrm{Re}[f_1(0,0,1,0)]}{\mathcal{N}}. \tag{44}$$

Here, again the difference $\tilde{q}-\tilde{q}'$ in all terms is equal to $q_k=\pm 1$, which indicates coherent superposition of the final states of different symmetry.

The first term in the first line in Eq. (44) describes the known coherent photodissociation mechanism resulting in the production of the photofragment orientation with linearly polarized light in the absence of the Coriolis interactions.[6,13,26] An example of this mechanism, $\Sigma \rightarrow (\Pi,\Sigma) \rightarrow (\Pi,\Sigma)$, is schematically shown in Fig. 3(a). All other terms in Eq. (44) contain different contributions from the Coriolis interaction. The examples of the dissociation mechanisms corresponding to each of these term are schematically shown in Figs. 3(b)–3(g).

As known,[6,13] in the axial recoil approximation and in the absence of the Coriolis interactions, the anisotropy parameters γ_1 and γ_1' are proportional to the real and imaginary parts of the same dynamical function $f_1(1,0)$. This result can be easily seen from comparison of Eqs. (43) and (44) because $f_1(1,0,1,0)=f_1(1,0)$. However, as shown in Eqs. (43) and (44), beyond the axial recoil approximation, this relationship is not valid even in the absence of the contribution from the Coriolis interaction because the rotational factors at the first terms in Eqs. (43) and (44) differ from each other. Moreover, in presence of the Coriolis interactions, the anisotropy parameter γ_1' contains two additional terms in the two last lines in Eq. (44) which describe the photolysis mechanisms which do not contribute to the parameter γ_1 in Eq. (43).

Particularly, the term in the fifth line in Eq. (44) describes production of the photofragment orientation via optical excitation of the coherent superposition of two perpendicular transitions followed by the Coriolis nonadiabatic transition. An example of this dissociation mechanism is $\Sigma \rightarrow (\Pi,\Pi) \rightarrow (\Pi,\Sigma)$, which is schematically shown in Fig. 3(e). The term in the sixth line in Eq. (44) describes production of the photofragment orientation via incoherent optical excitation of a *parallel transition* followed by the Coriolis nonadiabatic transition. An example of this dissociation mechanism is $\Sigma \rightarrow \Sigma \rightarrow (\Pi,\Sigma)$, which is schematically shown in Fig. 3(d). Both dissociation mechanisms do not give contribution to the parameter γ_1' in the axial recoil approximation because the corresponding rotational factors $d^2_{12}(\gamma)$ and $d^2_{01}(\gamma)$ in Eq. (44) are equal to zero at $\gamma=0$.

3. Rank K=2

The rank $K=2$ state multipoles describe the photofragment alignment. There are in general five independent alignment anisotropy parameters, s_2, α_2, η_2, γ_2, and γ_2', describing angular dependence of the photofragment alignment. The photofragment recoil angular distribution corresponding to each of the parameter are tabulated in Refs. 8 and 13. The expressions for the $K=2$ anisotropy parameters in case of the fast photodissociation of a linear molecule as a function of the dynamical functions $f_K(q,q',\tilde{q},\tilde{q}')$ in the first-order approximation of the Coriolis interaction are given below.

Parameter s_2

$$s_2=\frac{f_2(0,0,0,0)+2f_2(1,1,1,1)}{V_2(j_A)\mathcal{N}} + \frac{f_2(0,0,1,1)+2f_2(1,1,0,0)+2f_2(1,1,2,2)}{V_2(j_A)\mathcal{N}}, \tag{45}$$

where $V_2(j_A)=5\{j_A(j_A+1)/[(2j_A+3)(2j_A-1)]\}^{1/2}$.

According to Eq. (45), the alignment anisotropy parameter s_2 does not depend on the angle γ.

The first term in Eq. (45) consists of two parts which describe incoherent optical excitation of a perpendicular and a parallel transition followed by the radial nonadiabatic interaction or no nonadiabatic interaction at all. This term represents the known mechanism of producing the photofragment alignment with linearly polarized photolysis light in the absence of the Coriolis interactions which is described elsewhere.[8,13] Examples of this mechanism, $\Sigma \rightarrow \Pi \rightarrow \Pi$ and $\Sigma \rightarrow \Sigma \rightarrow \Sigma$, are schematically shown in Figs. 1(a) and 1(b).

The second term in Eq. (45) consists of three parts which describe incoherent optical excitation of a perpendicular or a parallel transition followed by a Coriolis nonadiabatic transition. Examples of this mechanism, $\Sigma \rightarrow \Sigma \rightarrow \Pi$, $\Sigma \rightarrow \Pi \rightarrow \Sigma$, and $\Sigma \rightarrow \Pi \rightarrow \Delta$, are schematically shown in Figs. 1(c)–1(e).

Parameter α_2

$$\alpha_2=d^2_{00}(\gamma)\frac{f_2(1,1,1,1)-f_2(0,0,0,0)}{V_2(j_A)\mathcal{N}} + d^2_{00}(\gamma)\frac{f_2(1,1,0,0)+f_2(1,1,2,2)-2f_2(0,0,1,1)}{V_2(j_A)\mathcal{N}} + 2\sqrt{3}d^2_{01}(\gamma)\frac{\mathrm{Im}[f_2(1,0,0,0)+f_2(1,0,1,1)]}{V_2(j_A)\mathcal{N}} - \sqrt{6}d^2_{02}(\gamma)\frac{f_2(1,-1,0,0)}{V_2(j_A)\mathcal{N}}. \tag{46}$$

The terms in the first two lines in Eq. (46) contain the same dynamical functions as in Eq. (45); however, the linear combinations of the dynamical functions here differ from that in Eq. (45).

The terms in the third and fourth lines in Eq. (46) describe coherent optical excitation of two transitions of different/same symmetry followed by a Coriolis nonadiabatic transition. The examples of such a mechanism, $\Sigma \rightarrow (\Pi,\Sigma) \rightarrow \Sigma$, $\Sigma \rightarrow (\Pi,\Sigma) \rightarrow \Pi$, and $\Sigma \rightarrow (\Pi,\Pi) \rightarrow \Sigma$, are shown in Figs. 2(a)–2(c).

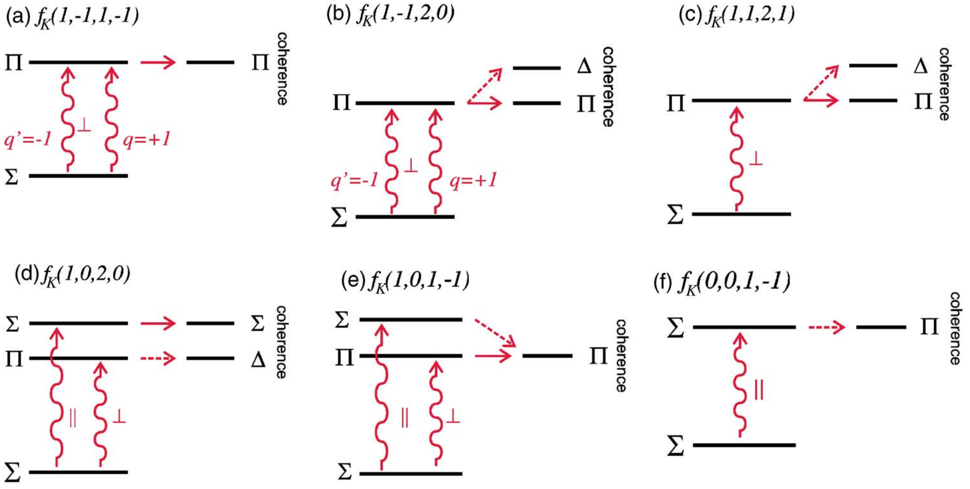

FIG. 4. (Color online) [(a)–(f)] Examples of dissociation mechanisms resulting in $\Delta\Omega=\pm 2$ coherent superposition of the final states. The notations are the same as in Fig. 1. These dissociation mechanisms can contribute to the anisotropy parameter η_K of the rank $K\geqslant 2$.

Parameter γ_2

$$\gamma_2 = 2\sqrt{3}d^2_{11}(\gamma)\frac{\mathrm{Re}[f_2(1,0,1,0)]}{V_2(j_A)\mathcal{N}} + 2\sqrt{3}d^2_{11}(\gamma)\frac{\mathrm{Re}[f_2(1,0,0,-1)+f_2(1,0,2,1)]}{V_2(j_A)\mathcal{N}} + 2\sqrt{3}d^2_{1-1}(\gamma)\frac{\mathrm{Re}[f_2(0,1,1,0)]}{V_2(j_A)\mathcal{N}} + 2d^2_{10}(\gamma)\frac{\mathrm{Im}[2f_2(0,0,1,0)-f_2(1,1,1,0)]}{V_2(j_A)\mathcal{N}} - 2d^2_{10}(\gamma)\frac{\mathrm{Im}[f_2(1,1,2,1)]}{V_2(j_A)\mathcal{N}} + 2\sqrt{6}d^2_{12}(\gamma)\frac{\mathrm{Im}[f_2(1,-1,1,0)]}{V_2(j_A)\mathcal{N}}. \tag{47}$$

The first term in Eq. (47) describes coherent optical excitation of a perpendicular and a parallel transition followed by the radial nonadiabatic interaction or no nonadiabatic interaction. The contribution from this term to the photofragment alignment is well known.[13,16] An example of this dissociation mechanism is the same as for the first term in Eq. (43). All other terms contain the Coriolis interactions. The corresponding dissociation mechanisms were already discussed after Eqs. (43) and (44) and schematically shown in Fig. 3. In all terms in Eq. (47), the index $q_k=\tilde{q}-\tilde{q}'$ is equal to 1.

Parameter γ'_2

$$\gamma'_2 = 2\sqrt{3}d^1_{11}(\gamma)\frac{\mathrm{Im}[f_2(1,0,1,0)]}{V_2(j_A)\mathcal{N}} + 2\sqrt{3}d^1_{11}(\gamma)\frac{\mathrm{Im}[f_2(1,0,0,-1)+f_2(1,0,2,1)]}{V_2(j_A)\mathcal{N}} + 2\sqrt{3}d^1_{1-1}(\gamma)\frac{\mathrm{Im}[f_2(0,1,1,0)]}{V_2(j_A)\mathcal{N}} + 2\sqrt{3}d^1_{10}(\gamma)\frac{\mathrm{Re}[f_2(1,1,1,0)+f_2(1,1,2,1)]}{V_2(j_A)\mathcal{N}}. \tag{48}$$

The parameter γ'_2 can contribute to the photofragment alignment off-diagonal matrix elements $\rho^{(j_A)}_{21}(\theta,\phi)$ and $\rho^{(j_A)}_{22}(\theta,\phi)$ only in the case if the photolysis light is circularly polarized.[5] To the best of our knowledge, this parameter has never been determined from experiment.

Parameter η_2

$$\eta_2 = \sqrt{6}d^2_{22}(\gamma)\frac{f_2(1,-1,1,-1)}{V_2(j_A)\mathcal{N}} + \sqrt{6}d^2_{22}(\gamma)\frac{f_2(1,-1,2,0)}{V_2(j_A)N} + 2d^2_{20}(\gamma)\frac{f_2(0,0,1,-1)-\mathrm{Re}\,f_2(1,1,2,0)}{V_2(j_A)\mathcal{N}} - 2\sqrt{3}d^2_{21}(\gamma)\frac{\mathrm{Im}[f_2(1,0,2,0)+f_2(1,0,1,-1)]}{V_2(j_A)\mathcal{N}}. \tag{49}$$

The first term in Eq. (49) describes coherent optical excitation of two perpendicular transitions followed by the radial nonadiabatic interaction or no nonadiabatic interaction. The contribution from this term to the photofragment alignment was studied by many authors.[13,16,37] An example of this dissociation mechanism is $\Sigma\to(\Pi,\Pi)\to(\Pi,\Pi)$, which is schematically shown in Fig. 4(a). All other terms contain the Coriolis interactions. The corresponding dissociation mechanisms are shown in Figs. 4(b)–4(f). In all the terms in Eq. (47), the index $q_k=\tilde{q}-\tilde{q}'$ is equal to 2.

The expressions for the anisotropy parameters of the high-rank ($K>2$) can be readily obtained by comparison of Eq. (37) with the corresponding state multipole expressions in Refs. 33 and 35.

IV. SLOW PREDISSOCIATION

In the limit of slow predissociation, a molecule executes many periods of rotation during its lifetime. The photofragment orbital polarization in this process has recently been studied by Kuznetsov and Vasyutinskii[31] for the case when the Coriolis interactions can be neglected. In the limit of slow predissociation, the excited states J, J' coherence can be neglected and only the terms with $J=J'$ in Eq. (25) describing the incoherent excitation of single rotational states should be taken into account. In this paper, we will consider the general case of the slow predissociation and assume the

TABLE I. Reduction factors $\langle d^{k_d}_{q_k Q'}(\gamma)\rangle$ of the rank $k_d=1$.

	Q'		
q_k	1	0	−1
1	$\frac{1}{2}$	0	$\frac{1}{2}$
0	0	0	0
−1	$\frac{1}{2}$	0	$\frac{1}{2}$

broad band excitation of the parent molecule which implies simultaneous excitation of the P, Q, and R rotational branches.

After summation over the values of the total angular momentum $J=J'$ in Eq. (25) in the high-J limit, the expression for the photofragment state multipoles can be presented in the form similar to Eq. (32) or (37), where the *rotational factors* $D^{k_d}_{q_k Q'}(\pi/2,\gamma,-\pi/2)$ are replaced by the *reduction factors* $\tau_{\text{red}}=d^{k_d}_{q_k 0}(\pi/2)d^{k_d}_{Q'0}(\pi/2)$, which are the product of two Wigner d functions[44] of rank k_d and argument $\pi/2$. As can be readily proved, each reduction factor is equal to the corresponding rotational factor averaged over the angle γ:

$$\tau_{\text{red}}=\frac{1}{2\pi}\int_0^{2\pi}D^{k_d}_{q_k Q'}\left(\frac{\pi}{2},\gamma,-\frac{\pi}{2}\right)d\gamma. \tag{50}$$

The Coriolis interactions are taken into account by the off-diagonal $Q'\neq q_k$ terms in Eqs. (32) and (37). If only radial nonadiabatic interactions are taken into account, then $Q'=q_k$ and the reduction factors τ_{red} become equivalent to the reduction factors $[d^{k_d}_{Q'Q'}(\pi/2)]^2$ introduced in Ref. 31.

Careful analysis of Eq. (37) shows that in the case of slow predissociation, the expression for the photofragment state multipoles in terms of the anisotropy parameters can be written in the form tabulated in Refs. 8, 13, and 32–34 where the corresponding anisotropy parameters of the rank $K=0,1,2$ can be obtained by averaging of Eqs. (41)–(49) over the angle γ as in Eq. (50). Therefore, in the case of slow predissociation, the contribution of different excitation mechanisms to the anisotropy parameters discussed above can be obtained by replacing in Eqs. (41)–(49) the corresponding d functions $d^{k_d}_{q_k Q'}(\gamma)$ by their values $\langle d^{k_d}_{q_k Q'}(\gamma)\rangle$ averaged over the angle γ.

The reduction factors $\langle d^{k_d}_{q_k Q'}(\gamma)\rangle$ for all possible values of the indices Q' and q_k are given in Tables I and II for $k_q=1$ and $k_q=2$, respectively. As can be seen from the tables, all reduction factors are smaller than unity and some of them are equal to zero. This means that the rotation of the molecular axis in the case of slow predissociation in general decreases the contribution from all excitation mechanisms shown in Eqs. (41)–(49). The only exception is the anisotropy parameter s_2 in Eq. (45) which does not depend on the molecular axis rotation.

As can be seen from Eqs. (41)–(49), in the presence of the Coriolis interactions, the anisotropy parameters cannot be classified in accordance with their "parallel" and "perpendicular" characters. However, they can be classified in accordance with the value of the quantum number q_k which is the projection of the spherical tensor ranks K and k_d onto the recoil direction, as shown in the next section.

V. PHOTOLYSIS OF AN ARBITRARY MOLECULE

As can be seen from Eqs. (25) and (32), each of these expressions can be formally presented in the same form:

$$\rho^{(j_A)}_{KQ}(\hat{\mathbf{k}},\mathbf{e})=\frac{1}{4\pi\sqrt{2j_A+1}}\sum_{k_d,q_d}\sum_{q_k}\mathbf{c}^K_{k_dq_k}E_{k_dq_d}(\mathbf{e})\times D^{K*}_{Qq_k}(\phi,\theta,0)D^{k_d}_{q_dq_k}(\phi,\theta,0), \tag{51}$$

where $\mathbf{c}^K_{k_dq_k}$ are coefficients describing the photodissociation dynamics and the angles specifying the direction of the light polarization vector $\mathbf{e}(\vartheta,\varphi)$ are expressed in the *laboratory* frame. The explicit form of these coefficients is of course not the same for Eqs. (25) and (32) and can be readily obtained from these expressions.

After transformation of the tensors $\rho^{(j_A)}_{KQ}(\hat{\mathbf{k}},\mathbf{e})$ and $E_{k_dq_d}(\mathbf{e})$ from the laboratory frame to the recoil frame where the new axis Z' is parallel to the recoil vector $\hat{\mathbf{k}}$, Eq. (51) can be simplified to the form

$$\rho^{(j_A)}_{Kq_k}(\mathbf{e})=\frac{1}{4\pi\sqrt{2j_A+1}}\sum_{k_d}\mathbf{c}^K_{k_dq_k}E_{k_dq_k}(\mathbf{e}), \tag{52}$$

where the angles specifying the direction of the light polarization vector $\mathbf{e}(\vartheta_k,\varphi_k)$ are now expressed in the *recoil* frame.

The recoil frame state multipoles $\rho^{(j_A)}_{Kq_k}(\mathbf{e})$ in Eq. (52), are not exactly the same with the molecular frame state multipoles used in Ref. 8 and 13, as they are normalized to the total number of photofragments: $\langle\rho^{(j_A)}_{00}\rangle=1/\sqrt{2j_A+1}$, whereas the molecular frame state multipoles in Refs. 8 and 13 are normalized to the number of photofragments scattered into the recoil direction: $\rho^{(j_A)}_{00}(\theta,\phi)$. Also, the values of the mo-

TABLE II. Reduction factors $\langle d^{k_d}_{q_k Q'}(\gamma)\rangle$ of the rank $k_d=2$.

	Q'				
q_k	2	1	0	−1	−2
2	$\frac{3}{8}$	0	$\frac{\sqrt{3}}{4\sqrt{2}}$	0	$\frac{3}{8}$
1	0	0	0	0	0
0	$\frac{\sqrt{3}}{4\sqrt{2}}$	0	$\frac{1}{4}$	0	$\frac{\sqrt{3}}{4\sqrt{2}}$
−1	0	0	0	0	0
−2	$\frac{3}{8}$	0	$\frac{\sqrt{3}}{4\sqrt{2}}$	0	$\frac{3}{8}$

lecular frame state multipoles are given in Refs. 8 and 13 for the particular case when the light polarization vector **e** is parallel to the laboratory axis Z.

Equation (52) can be treated as an expansion of the photofragment state multipole $\rho_{Kq_k}^{(j_A)}(\mathbf{e})$ over the photolysis light polarization tensors $E_{k_d q_k}(\mathbf{e})$; both spherical tensors are quantized onto the recoil vector $\hat{\mathbf{k}}$. The projection q_k in Eq. (52) is preserved because the right-hand part of Eq. (52) must behave under transformation of the coordinate frame as a spherical tensor of the rank K and projection q_k; however, the coefficients $\mathbf{c}_{k_d q_k}^{K} \sim \langle \rho_{Kq_k}^{(j_A)} E_{k_d q_k} \rangle$ are scalar values which do not depend on the vector **e**.

The expansion coefficients $\mathbf{c}_{k_d q_k}^{K}$ can be used as a set of universal *anisotropy-transforming* coefficients describing the photodissociation dynamics. The total number of these coefficients can be easily calculated for any particular case because the rank K ranges from $K=0$ to $K=2j_A$, the rank k_d is limited to the values $k_d=0,1,2$, and the projection q_k ranges from $q_k=-\min(k_d,K)$ to $q_k=\min(k_d,K)$. The set of the coefficients $\mathbf{c}_{k_d q_k}^{K}$ is an alternative to the set of the anisotropy parameters β, α_K, γ_K, γ'_K, s_K, and η_K.[8,32–34] Whereas the anisotropy parameters are all real and normalized to the orientation and alignment of the photofragments averaged over all recoil directions,[13] the coefficients $\mathbf{c}_{k_d q_k}^{K}$ are in general complex. The value of the zero-rank coefficient $\mathbf{c}_{00}^{0}$ is chosen to provide the standard normalization condition for the state multipoles in Eqs. (51) and (52): $\langle \rho_{00}^{(j_A)} \rangle = 1/(2j_A+1)^{1/2}$.

It is easy to show from Eq. (52) using the properties of the spherical tensors that the coefficients $\mathbf{c}_{k_d q_k}^{K}$ obey the following relation:

$$(\mathbf{c}_{k_d q_k}^{K})^{*} = \mathbf{c}_{k_d -q_k}^{K}. \tag{53}$$

The relationship between the coefficients $\mathbf{c}_{k_d q_k}^{K}$ and the anisotropy parameters β, α_K, γ_K, γ'_K, s_K for $K=0,1,2$ is given in Table III. Similar relationship for the higher ranks $K=3,4$ can be readily obtained by using the definition of the corresponding anisotropy parameters[33,34] and Eq. (32). As shown in Table III, these two sets are simply proportional to each other in pairs; however, some of the coefficients $\mathbf{c}_{k_d q_k}^{K}$ have fixed values.

The tensor equation (52) holds in general because *any* spherical tensor $\rho_{Kq_k}^{(j_A)}$ which depends on the light polarization **e** can be expanded over the orthogonal light polarization spherical tensors $E_{k_d q_k}(\mathbf{e})$.

Therefore, Eq. (52) can be used for description of an arbitrary photodissociation reaction including photodissociation of a di- or a polyatomic molecule without reference to the photodissociation mechanism within the first-order time-dependent perturbation theory and in the case if the photolysis light is the only source of anisotropy in the reaction. However, the explicit values of the anisotropy-transforming coefficients $\mathbf{c}_{k_d q_k}^{K}$ depend on the parent molecule and on the photodissociation mechanism and should be either determined from experiment or calculated theoretically.

Therefore, the laboratory frame recoil-angle dependencies of different rank photofragment state multipoles have the same universal form (51) for any photodissociation process within the above conditions. The anisotropy parameters β, α_K, γ_K, γ'_K, s_K, and η_K fully characterize the process dynamics and can be determined from experiment as phenomenological coefficients at the kinematical (recoil-angle dependent) parts of the photofragment state multipoles $\rho_{KQ}^{(j_A)}(\theta,\phi)$. These dependencies are tabulated in Refs. 13, 33, and 34. In general, the anisotropy parameters depend on the ranks K, k_q, and their projection onto the recoil axis q_k.

TABLE III. Relationship between the anisotropy-transforming coefficients $\mathbf{c}_{k_d q_k}^{K}$ and the anisotropy parameters. The coefficients $V_2(j)$ are equal to $V_2(j)=5[j(j+1)/(2j+3)(2j-1)]^{1/2}$.

$\mathbf{c}_{k_d q_k}^{K}$	Anisotropy parameter expression
$\mathbf{c}_{00}^{0}$	$-\sqrt{3}$
$\mathbf{c}_{10}^{0}$	0
$\mathbf{c}_{20}^{0}$	$\sqrt{\frac{3}{2}}\beta$
$\mathbf{c}_{00}^{1}$	0
$\mathbf{c}_{10}^{1}$	$3\sqrt{6}\alpha_1$
$\mathbf{c}_{11}^{1}$	$3\sqrt{\frac{3}{2}}\gamma_1$
$\mathbf{c}_{20}^{1}$	0
$\mathbf{c}_{21}^{1}$	$-3i\sqrt{\frac{3}{2}}\gamma'_1$
$\mathbf{c}_{00}^{2}$	$-\sqrt{15}V_2(j_A)s_2$
$\mathbf{c}_{10}^{2}$	0
$\mathbf{c}_{11}^{2}$	$i\sqrt{\frac{15}{2}}V_2(j_A)\gamma'_2$
$\mathbf{c}_{20}^{2}$	$-\sqrt{30}V_2(j_A)\alpha_2$
$\mathbf{c}_{21}^{2}$	$-\sqrt{\frac{15}{2}}V_2(j_A)\gamma_2$
$\mathbf{c}_{22}^{2}$	$-\sqrt{\frac{15}{2}}V_2(j_A)\eta_2$

VI. CONCLUSION

Full quantum-mechanical expression for the photodissociation cross section where both radial and Coriolis nonadiabatic interactions are taken into account was derived by using *parity-adapted* representation of the molecular wavefunction. The obtained expression was simplified using the high-J quasiclassical approximation for two practically interesting cases: the fast photodissociation and the slow predissociation. As shown, in both cases, the angle-recoil distributions of the photofragment state multipoles have the same universal form in terms of the anisotropy parameters.

The expressions for the anisotropy parameters of the rank $K=0$, 1, and 2 which contain the dynamical functions responsible for different dissociation mechanisms are presented and analyzed. In particular, it was shown that the Coriolis interactions can result in the production of the photofragment orientation via pure parallel excitation of the parent molecule. In the case of direct photodissociation, the rotation of the molecular axis on the angle γ is described by the number of the rotation factors which depend on a particular dissociation mechanism and in general reduce the photofragment orientation and alignment. In the case of slow predissociation, the effect of rotation of the molecular axis is described by the set of reduction factors that can be obtained by averaging of the corresponding rotation factors over the angle γ. In the absence of the Coriolis interaction, the obtained results are equivalent to those obtained before.

The case of an arbitrary photodissociation process is discussed. As shown, for any photodissociation process, the recoil-angle dependence of the photofragment angular momentum polarization written in terms of the anisotropy parameters has the same form.

The results obtained in this paper can be used for interpretation of vector correlations in photodissociation experiments.

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APPENDIX A: EXPANSION OF THE DISSOCIATIVE WAVE FUNCTION

Following the approach described in Ref. 26, we derive the expansion of the asymptotic expression for the dissociative wavefunction and then construct the expression valid for any internuclear distance. We start from the asymptotic expression given by Eq. (A4) in Ref. 26 which is the expansion over the *diabatic* molecular basis:

$$\begin{aligned} e^{i\mathbf{kR}}|jm\rangle + \sum_{j'm'} f_{j'm'jm}(\hat{\mathbf{R}};\hat{\mathbf{k}})\frac{e^{-ik'_{j'}R}}{R}|j'm'\rangle \\ = -\frac{4\pi^2 i}{R}\sum_{J,M}\sum_{\Omega_R,\Omega_k}\sum_{j'}\frac{e^{i(\pi/2)J}}{\sqrt{kk'}} \\ \times[\delta_{\Omega_R,\Omega_k}\delta_{j,j'}e^{i(kR-(\pi/2)J)} - S^J_{j'\Omega_R j\Omega_k}e^{-i(k'R-\pi/2J)}] \\ \times\frac{2J+1}{4\pi}D^J_{M\Omega_k}(\phi_k,\theta_k,0)D^{j*}_{m\Omega_k}(\phi_k,\theta_k,0) \\ \times D^{J*}_{M\Omega_R}(\phi_R,\theta_R,0)|j'\Omega_R\rangle, \end{aligned} \tag{A1}$$

where $|j'\Omega_R\rangle$ is the *diabatic* molecular wavefunction projected onto the direction of the molecular axis, and $S^J_{j'\Omega_R j\Omega_k}$ is the scattering matrix in the diabatic representation

$$S^J_{j'\Omega_R j\Omega_k} = \langle j'\Omega_R|S^J|j\Omega_k\rangle. \tag{A2}$$

The asymptotical ($R\to\infty$) wavefunctions in the μ representation $\Psi^{JM\mu}_{j\lambda}$ have the same form as Eq. (6) but with $|n\lambda\rangle$ replaced by $|j\lambda\rangle$. The terms in Eq. (A1) are transformed by using

$$t_\lambda\sqrt{\frac{2J+1}{4\pi}}D^{J*}_{M\lambda}(\hat{\mathbf{R}},0)|j\lambda\rangle = \frac{1}{2}\sum_\mu \Psi^{JM\mu}_{j\lambda} \tag{A3}$$

$$t_\lambda\sqrt{\frac{2J+1}{4\pi}}D^{J*}_{M-\lambda}(\hat{\mathbf{R}},0)|j-\lambda\rangle = \frac{1}{2}\sum_\mu \mu(-1)^{J-\varphi}\Psi^{JM\mu}_{j\lambda}. \tag{A4}$$

By using the scattering matrix in the $\lambda\mu$ representation (note that the scattering matrix is diagonal over μ), one obtains

$$\begin{aligned} e^{i\mathbf{kR}}|jm\rangle + \sum_{j'm'} f_{j'm'jm}(\hat{\mathbf{R}};\hat{\mathbf{k}})\frac{e^{-ik'_{j'}R}}{R}|j'm'\rangle \\ = -\frac{4\pi^2 i}{R}\sum_{J,M,\mu}\sum_{\lambda_R,\lambda_k}\sum_{j'}\frac{e^{i(\pi/2)J}}{\sqrt{kk'}}[\delta_{\lambda_R,\lambda_k}\delta_{j,j'}e^{i(kR-(\pi/2)J)} \\ - S^{J\mu}_{j'\lambda_R j\lambda_k}e^{-i(k'R-(\pi/2)J)}]\Psi^{JM\mu}_{j'\lambda_R}\Phi^{JM\mu}_{jm\lambda_k}(\hat{\mathbf{k}}), \end{aligned} \tag{A5}$$

where

$$\begin{aligned} \Phi^{JM\mu}_{jm\lambda_k}(\hat{\mathbf{k}}) = t_{\lambda_k}\sqrt{\frac{2J+1}{4\pi}}(D^J_{M\lambda_k}(\hat{\mathbf{k}},0)D^{j*}_{m\lambda_k}(\hat{\mathbf{k}},0) \\ + \mu(-1)^{J-\varphi_k}D^J_{M-\lambda_k}(\hat{\mathbf{k}},0)D^{j*}_{m-\lambda_k}(\hat{\mathbf{k}},0)). \end{aligned} \tag{A6}$$

Now one should expand the dissociative wavefunction over the *adiabatic* basis (6) built on the adiabatic electronic terms $|n\Omega\rangle$. The transformation coefficient from diabatic to adiabatic function is clearly

$$\langle\Psi^{JM\mu}_{j\lambda}|\Psi^{JM\mu}_{n\lambda}\rangle = \langle j\lambda|n\lambda\rangle, \tag{A7}$$

where $\langle j\lambda|n\lambda\rangle$ is an expansion coefficient in the asymptotic $R\to\infty$ region; it is related to the $\mathcal{T}$ coefficients in Eq. (10) as

$$\langle j\Omega|n\Omega\rangle = \sum_{\Omega_A\Omega_B}\mathcal{T}^{n\Omega}_{j_A\Omega_A j_B\Omega_B}C^{j\Omega}_{j_A\Omega_A j_B\Omega_B}. \tag{A8}$$

The scattering matrix should also be transformed to the adiabatic representation

$$S^{J\mu}_{n_R\lambda_R;n_k\lambda_k} = \sum_{j'j''}\langle n_R\lambda_R|j'\lambda_R\rangle S^{J\mu}_{j'\lambda_R j''\lambda_k}\langle j''\lambda_k|n_k\lambda_k\rangle. \tag{A9}$$

After producing projection summations, one obtains the asymptotical expression for the scattering wavefunction:

$$\begin{aligned} e^{i\mathbf{kR}}|jm\rangle + \sum_{j'm'} f_{j'm'jm}(\hat{\mathbf{R}};\hat{\mathbf{k}})\frac{e^{-ik'_{j'}R}}{R}|j'm'\rangle \\ = -\frac{4\pi^2 i}{R}\sum_{J,M,\mu}\sum_{\lambda_R,\lambda_k}\sum_{n_R n_k}\frac{e^{i(\pi/2)J}}{\sqrt{kk'}}[\delta_{\lambda_R,\lambda_k}\delta_{n_R,n_k}e^{i(kR-(\pi/2)J)} \\ - S^{J\mu}_{n_R\lambda_R;n_k\lambda_k}e^{-i(k'R-(\pi/2)J)}]\Psi^{JM\mu}_{n_R\lambda_R}\Phi^{JM\mu}_{jm\lambda_k}(\hat{\mathbf{k}})\langle n_k\lambda_k|j\lambda_k\rangle. \end{aligned} \tag{A10}$$

By using Eqs. (A8) and (A10), the expansion of the dissociative wavefunction at any internuclear distance is finally written in the form of Eq. (13), where scattering function $\chi^{J\mu}_{n_R\lambda_R;n_k\lambda_k}(R)$ has the asymptotic form as Eq. (15).

APPENDIX B: DERIVATION OF THE SCATTERING EQUATION

The derivation of the scattering equation is proceeded by using the orthogonality properties of expansion (13). We multiply Eq. (19) by the $(\Phi^{JM\mu}_{jmn_k\lambda_k}(\hat{\mathbf{k}}))^*\langle\Psi^{JM}_{n''\lambda'_R\mu}|$, integrate over $\hat{\mathbf{R}}$ and $\mathbf{r}$, and summate over m and j. It allows one to select terms with particular values of J, M, μ, n, and λ_k and obtain the equation for the scattering functions $\chi^{J\mu}_{n'\lambda_R n\lambda_k}(R)$.

The pure orbital part of the Hamiltonian (taken as operator acting on the $R\Psi$) could be presented as a sum of the radial and Coriolis parts:

$$\hat{\mathcal{H}}_R = \left(-\frac{1}{2\mu_f}\frac{\partial^2}{\partial R^2} + \frac{1}{2\mu_f R^2}(\hat{J}^2 + \hat{j}_{x'}^{\,2} + \hat{j}_{y'}^2 - \hat{j}_{z'}^2)\right), \tag{B1}$$

$$\hat{\mathcal{H}}_C = -\frac{1}{2\mu_f R^2}(\hat{\mathbf{J}}\hat{\mathbf{j}} + \hat{\mathbf{j}}\hat{\mathbf{J}} - 2\hat{j}_{z'}^2), \tag{B2}$$

where x', y', and z' select components of the electronic angular momentum in the molecular coordinate system. Substituting the expressions for the Hamiltonian in the Schrödinger equation and applying the symmetry properties of Wigner D functions and molecular wavefunctions, one obtains Eq. (21).

APPENDIX C: THE PHOTODISSOCIATION CROSS SECTION

After substitution of the wavefunction expansion (13) into the general expression for the dissociation cross section Eq. (3), one obtains

$$\begin{aligned}\sigma_{KQ} \propto & \sum_{j,m,j',m',j_B} (-1)^{j_B+j} e^{i(\pi/2)(J-J')}[(2K+1)(2j+1)]^{1/2} C^{j'm'}_{jmK-Q}\begin{Bmatrix} j_A & j_A & K \\ j' & j & j_B\end{Bmatrix}\\
&\times \sum_{J,M,\mu}\sum_{J',M',\mu'}\sum_{n_k,\lambda_k,n_k',\lambda_k'}(\Phi^{J'M'\mu'}_{j'm'n_k'\lambda_k'}(\hat{\mathbf{k}}))^*\Phi^{JM\mu}_{jmn_k\lambda_k}(\hat{\mathbf{k}})\sum_{n_R,\lambda_R,n_R'\lambda_R'}\sum_{\mu_i}\left\langle \frac{1}{R}\chi^{J'\mu'}_{n_R'\lambda_R' n_k'\lambda_k'}(R)\Psi^{J'M'\mu'}_{n_R'\lambda_R'}|\hat{\mathbf{d}}\cdot\mathbf{e}|\chi_i(R)\Psi^{J_iM_i\mu_i}_{n_i\lambda_i}\right\rangle\\
&\times\left\langle \frac{1}{R}\chi^{J\mu}_{n_R\lambda_R n_k\lambda_k}(R)\Psi^{JM\mu}_{n_R\lambda_R}|\hat{\mathbf{d}}\cdot\mathbf{e}|\chi_i(R)\Psi^{J_iM_i\mu_i}_{n_i\lambda_i}\right\rangle^*.\end{aligned} \tag{C1}$$

We will refer to the part of Eq. (C1) from the beginning til the product of the wave functions $(\Phi^{J'M'\mu'}_{j'm'n_k'\lambda_k'})^*\Phi^{JM\mu}_{jmn_k\lambda_k}$ as the kinematical part of the cross section and to the rest of the terms as the dynamical part. The summation over m,m' in the kinematical part could be carried out by using the Clebsch–Gordan series of the D-function product:

$$\begin{aligned}&\sum_{j'm'jm}(-1)^{j_B+j}[(2K+1)(2j+1)]^{1/2}C^{j'm'}_{jmK-Q}\begin{Bmatrix} j_A & j_A & K \\ j' & j & j_B\end{Bmatrix}(\Phi^{J'M'\mu'}_{j'm'n_k'\lambda_k'})^*\Phi^{JM\mu}_{jmn_k\lambda_k}\\
&\quad=\sum_{\Omega_A\Omega_B\Omega_A'\Omega_B'}\sum_{j'j}(-1)^{j_B+\Omega_k'-Q}[(2j'+1)(2j+1)]^{1/2}C^{Kq_k}_{j\Omega_k j'-\Omega_k'}C^{j\Omega_k}_{j_A\Omega_A j_B\Omega_B}C^{j'\Omega_k'}_{j_A\Omega_A' j_B\Omega_B'}\\
&\quad\times\begin{Bmatrix} j_A & j_A & K \\ j' & j & j_B\end{Bmatrix}\frac{\sqrt{(2J+1)(2J'+1)}}{4\pi}D^{K*}_{Qq_k}(\hat{\mathbf{k}},0)D^{J}_{M\Omega_k}(\hat{\mathbf{k}},0)D^{J'*}_{M'\Omega_k'}(\hat{\mathbf{k}},0)t_{\lambda_k}t_{\lambda_k'}(\mathcal{T}^{n_k'\lambda_k'}_{j_A\Omega_A'j_B\Omega_B'}+\mu'(-1)^{J'-\phi_{k'}}\mathcal{T}^{n_k'-\lambda_k'}_{j_A\Omega_A'j_B\Omega_B'})\\
&\quad\times(\mathcal{T}^{n_k\lambda_k}_{j_A\Omega_Aj_B\Omega_B}+\mu(-1)^{J-\phi_k}\mathcal{T}^{n_k-\lambda_k}_{j_A\Omega_Aj_B\Omega_B})^*.\end{aligned} \tag{C2}$$

The further j,j' summation is done by using the summation rule for $6-j$ symbols:[44]

$$\sum_{j'j}\sqrt{(2j'+1)(2j+1)}C^{Kq_k}_{j\Omega_k j'-\Omega_k'}C^{j\Omega_k}_{j_A\Omega_Aj_B\Omega_B}C^{j'\Omega_k'}_{j_A\Omega_A'j_B\Omega_B'}\begin{Bmatrix} j_A & j_A & K \\ j' & j & j_B\end{Bmatrix} = (-1)^{-j_B-\Omega_B}C^{Kq_k}_{j_A-\Omega_A'j_A\Omega_A}\delta_{\Omega_B,\Omega_B'}. \tag{C3}$$

The dipole moment matrix element in the dynamical part of the cross section could be expressed as

$$\begin{aligned}\langle\Psi^{JM\mu}_{n_R\lambda_R}|\hat{\mathbf{d}}\cdot\mathbf{e}|\Psi^{J_iM_i\mu_i}_{n_i\lambda_i}\rangle &= \sum_{p,q}(-1)^p e_{-p}\langle\Psi^{JM\mu}_{n_R\lambda_R}|D^{1*}_{pq}\hat{d}_q|\Psi^{J_iM_i\mu_i}_{n_i\lambda_i}\rangle\\
&=\sum_{p,q}(-1)^p e_{-p}t_{\lambda_R}t_{\lambda_i}\sqrt{\frac{2J_i+1}{2J+1}}C^{JM}_{J_iM_i1p}[C^{J\lambda_R}_{J_i\lambda_i1q}\langle n_R\lambda_R|\hat{d}_q|n_i\lambda_i\rangle+\mu(-1)^{J-\phi_R}C^{J-\lambda_R}_{J_i\lambda_i1q}\langle n_R-\lambda_R|\hat{d}_q|n_i\lambda_i\rangle\\
&\quad+\mu_i(-1)^{J_i-\phi_i}C^{J\lambda_R}_{J_i-\lambda_i1q}\langle n_R\lambda_R|\hat{d}_q|n_i-\lambda_i\rangle+\mu\mu_i(-1)^{J+J_i-\phi_R-\phi_i}C^{J-\lambda_R}_{J_i-\lambda_i1q}\langle n_R-\lambda_R|\hat{d}_q|n_i-\lambda_i\rangle].\end{aligned} \tag{C4}$$

By replacing $q \to -q$ in the last two terms and using the symmetry relation

$$\langle n_R - \lambda_R | \hat{d}_{-q} | n_i - \lambda_i \rangle = (-1)^{\phi_R - \phi_i} \langle n_R \lambda_R | \hat{d}_q | n_i \lambda_i \rangle, \tag{C5}$$

one obtains

$$\begin{aligned} &\langle \Psi^{JM\mu}_{n_R\lambda_R} | \hat{\mathbf{d}} \cdot \mathbf{e} | \Psi^{J_iM_i\mu_i}_{n_i\lambda_i} \rangle \\ &\quad = \sum_{p,q} (-1)^p e_{-p} \sqrt{\frac{2J_i+1}{2J+1}} C^{JM}_{J_iM_i1p} \delta_{\mu,-\mu_i} \\ &\qquad \times 2t_{\lambda_R} t_{\lambda_i} [C^{J\lambda_R}_{J_i\lambda_i1q} \langle n_R\lambda_R | \hat{d}_q | n_i\lambda_i \rangle \\ &\qquad + \mu(-1)^{J-\phi_R} C^{J-\lambda_R}_{J_i\lambda_i1q} \langle n_R - \lambda_R | \hat{d}_q | n_i\lambda_i \rangle], \end{aligned} \tag{C6}$$

where the parity-selection factor $(1-\mu\mu_i)=2\delta_{\mu,-\mu_i}$ has automatically appeared. Finally, by producing Clebsch–Gordan series for the Wigner D functions in the expression for the cross section and summating over projections M, M', M_i using

$$\begin{aligned} &\sum_{MM'M_i} C^{JM}_{J_iM_i1p} C^{J'M'}_{J_iM_i1p'} D^J_{M\Omega_k}(\hat{\mathbf{k}},0) D^{J'*}_{M'\Omega'_k}(\hat{\mathbf{k}},0) \\ &\quad = \sum_{k_d(q_d)} (-1)^{\Omega'_k} D^{k_d}_{q_dq_k}(\hat{\mathbf{k}},0) C^{k_dq_k}_{J\Omega_kJ'-\Omega'_k} \\ &\qquad \times \sum_{MM'M_i} (-1)^{-M'} C^{JM}_{J_iM_i1p} C^{J'M'}_{J_iM_i1p'} C^{k_dq_q}_{JMJ'-M'} \\ &\quad = \sum_{k_d(q_d)} (-1)^{\Omega'_k+J+J'-J_i-p'} D^{k_d}_{q_dq_k}(\hat{\mathbf{k}},0) C^{k_dq_k}_{J\Omega_kJ'-\Omega'_k} \\ &\qquad \times \sqrt{(2J+1)(2J'+1)} C^{k_dq_d}_{1-p'1p} \begin{Bmatrix} J' & J & k_d \\ 1 & 1 & J_i \end{Bmatrix}, \end{aligned} \tag{C7}$$

one obtains expression (25). Note that summation over p and p' is hidden inside the light density matrix.

APPENDIX D: SUMMATION OVER J, J' VALUES IN THE HIGH-J LIMIT

The summation procedure over high-J values in quasiclassical approximation is described in detail by Kuznetsov and Vasyutinskii.[26] In the parity-adapted approach, some modifications are necessary.

The part of the cross section that depends on J and J' could be presented as a sum of the terms of the following form:

$$\begin{aligned} S_{\alpha\alpha'} = &\sum_{J,J'} e^{i\gamma(J-J')} (-1)^{J+J'+\alpha J+\alpha' J'} \sqrt{(2J+1)(2J'+1)} \\ &\times \begin{Bmatrix} J' & J & k_d \\ 1 & 1 & J_i \end{Bmatrix} \\ &\times C^{k_dq_k}_{J(\Omega_A+\Omega_B)J'-(\Omega'_A+\Omega_B)} C^{J'\Omega'_R}_{J_i\lambda_i1q'} C^{J\Omega_R}_{J_i\lambda_i1q}, \end{aligned} \tag{D1}$$

where α, α' are non-negative integer numbers. The different values of α, α' arise from $(-1)^J$ phase factors before coefficients $\mathcal{T}^{n_k-\lambda_k}_{j_A\Omega_Aj_B\Omega_B}$ in Eq. (25) and from the similar factors in the scattering wavefunctions in Eq. (18). In the high-J limit, one can use asymptotic expressions for vector coefficients:[44]

$$\begin{Bmatrix} J' & J & k_d \\ 1 & 1 & J_i \end{Bmatrix} \approx \frac{(-1)^{k+k'}}{\sqrt{2J_i(2k_d+1)}} C^{k_d(k'-k)}_{1-k1k'}, \tag{D2}$$

$$C^{J\Omega_R}_{J_i\lambda_i1q} \approx \delta_{\Omega_R,q+\lambda_i} D^1_{qk}\left(0,\frac{\pi}{2},0\right), \tag{D3}$$

$$\begin{aligned} &C^{k_dq_k}_{J(\Omega_A+\Omega_B)J'-(\Omega'_A+\Omega_B)} \\ &\quad \approx (-1)^{k+J_i-\Omega_A-\Omega_B} \sqrt{\frac{2k_d+1}{2J_i}} \delta_{q_k,\Omega_A-\Omega'_A} \\ &\qquad \times D^{k_d}_{-q_k(k'-k)}\left(0,\frac{\pi}{2},0\right), \end{aligned} \tag{D4}$$

where $k=J-J_i$ and $k'=J'-J_i$. The expression for the $S_{\alpha\alpha'}$ reduces to

$$\begin{aligned} S_{\alpha\alpha'} = &(-1)^{(\alpha+\alpha'+3)J_i-\Omega_A-\Omega_B} \delta_{q_k,\Omega_A-\Omega'_A} \delta_{\Omega_R,q+\lambda_i} \delta_{\Omega'_R,q'+\lambda_i} \\ &\times \sum_{k,k'} e^{-i\gamma(k'-k)} (-1)^{(\alpha+1)k+\alpha'k'} C^{k_d(k'-k)}_{1-k1k'} \\ &\times D^1_{qk}\left(0,\frac{\pi}{2},0\right) D^1_{q'k'}\left(0,\frac{\pi}{2},0\right) D^{k_d}_{-q_k(k'-k)}\left(0,\frac{\pi}{2},0\right). \end{aligned} \tag{D5}$$

The summation is carried out using the following property of D functions:[44]

$$D^1_{q'k'}\left(0,\frac{\pi}{2},0\right) = (-1)^{1-k'} D^1_{-q'k'}\left(0,\frac{\pi}{2},0\right), \tag{D6}$$

α' times for k' and α times for k correspondingly. By using the Clebsch–Gordan series for D-function product and their unitary relation, one obtains

$$\begin{aligned} S_{\alpha\alpha'} = &(-1)^{(\alpha+\alpha'+3)J_i-\Omega_A-\Omega_B+\alpha+\alpha'+q} \delta_{q_k,\Omega_A-\Omega'_A} \delta_{\Omega_R,q+\lambda_i} \\ &\times \delta_{\Omega'_R,q'+\lambda_i} C^{k_d-Q'}_{1-(-1)^\alpha q1(-1)^{\alpha'}q'} D^{k_d}_{-q_k-Q'}\left(\frac{\pi}{2},\gamma,-\frac{\pi}{2}\right). \end{aligned} \tag{D7}$$

Finally, one can transform the expression for the cross section to the form of Eq. (29) by changing where necessary $q' \to -q'$ and $q \to -q$ under summation and applying symmetry properties of molecular wave functions given in Eq. (C5).

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