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Spin polarization of molecular photoelectrons in the case of rotationally resolved photoionization spectra

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A theoretical derivation of the differential photoionization cross section taking into account the spin polarization of photoelectrons is presented. This cross section corresponds to rotationally resolved transitions from an initial rotational level of the neutral molecule to a final rotational level of the ion. The final-state wave function of the ion-plus-electron system is written in the Hund's-case (c) coupling scheme, and the parities of this state and of the initial-state wave functions are explicitly introduced. Two equivalent expressions for the cross section are obtained that correspond to two coupling schemes of the angular momenta involved in the problem. One is a transferred-momentum-coupling scheme, and the other is the final-state (ion-plus-electron) total-angular-momentum-coupling scheme. Their respective advantages in analyzing the experimental results are highlighted. Each term in the transition moment and cross-section expressions contains a multiplicative factor of a simple form that determines if a contribution to these expressions is zero or not, thus playing the role of a selection-rule factor. Our expressions apply to the single-photon process as well as to multiphoton processes in cases in which only the last (one-photon) ionization step is considered explicitly. The paper ends with derivation of explicit formulas for the total cross section and the angle-integrated spin-polarization parameter in a particular case. The photoionization of the HI molecule was the model for these particular formulas.

I. INTRODUCTION

The first measurements of the spin polarization of molecular photoelectrons were performed in the case of CO_2 and N_2O (Ref. 1) molecules less than ten years ago. Those experiments as well as subsequent ones were performed using synchrotron radiation as a source of light with moderate experimental resolution. Recently, vuv laser light sources were developed that allowed much better resolution in photoionization studies of molecules. In particular, for molecules with a relatively large rotational constant, this new technique makes it possible to distinguish between rotational branches of a resonance feature, as has been shown in the case of photoionization of HI by Huth *et al.*,[2] and Hart and Hepburn.[3] The experimental arrangements used by these authors provide high-resolution photoelectron-yield spectra giving the total cross section, angle-integrated photoelectron polarization parameter $\bar{P}$ or differential cross section without spin analysis. Simultaneous angle- and spin-resolved photoelectron yield spectra are, in principle, attainable with the present experimental setup. Using a threshold photoelectron spectrometer developed recently by Müller-Detlefs, Sander, and Schlag[4] or a time-of-flight electron spectrometer developed by Allendorf *et al.*[4] (which is not restricted to the threshold region) the rotational spectrum in the exit channel can be resolved. This progress in techniques indicates that rotational photoionization spectra (i.e., cross section, angular-integrated polarization parameter, and differential cross section) corresponding to the transition from a Boltzmann distribution of initial states to allowed final states can be obtained in the near future.

A different direction of research is multiphoton excitation and ionization.[5] With lasers of moderate power, and particularly using two lasers of different colors, this technique permits the preparation of an intermediate excited state of given rotational level and parity, which is then photoionized. By this technique, one can obtain rotational state-to-state photoionization spectra of an excited state.

At low photon energies a theory concerning spin polarization of photoelectrons ejected from atoms was developed nearly 20 years ago and is summarized in the book by Kessler[6] and in a review paper by one of us.[7] More recently the corresponding formulas appropriate for molecules have been derived.[8] In 1985 the first calculations of polarization parameters were published,[9] followed by a more detailed study in the case of shape resonances and Cooper minima in hydrogen halides.[10] In these papers molecular rotation has not been taken into account.

Several authors[11-19] have derived expressions for the differential cross section without taking into account the spin orientation of the photoelectron. The transferred momentum formulation of Sichel and co-workers,[11,12] Fano and Dill,[13] and Dill[14] has been used by, e.g., Raoult, Jungen, and Dill[15] in a calculation of rotationally resolved total and differential cross section of the H_2 molecule. The total angular momentum formulation developed by Tully, Berry, and Dalton[16] and Thiel[17] has been used in the calculation of angular distribution without rotation by many authors (see, e.g., Thiel[17]).

More recently, analogous formulations, including rotation, have been proposed by Itikawa[18] and Chandra.[19] None of the papers mentioned above[8-18] takes simultaneously into account rotation and spin.

The present work was motivated by the recent achievements of the experimental technique mentioned above. The high-resolution photoabsorption spectra of the HI molecule measured by Huth *et al.*[2] and Hart and Hepburn[3] were only roughly interpreted by these authors. Detailed theoretical analysis of the experimental results is difficult due to the fact that the existing model[8,9] ignores vibration and rotation. Vibrations imply changes in the dynamical part of the cross section, namely, in calculation of vibrationally resolved transition moments. No changes in the expressions for the total and differential cross sections themselves are needed. As a consequence, the vibration is not considered explicitly in this paper. Inclusion of the rotational degree of freedom implies changes in the coupling of angular momenta of the photoelectron and residual ion, which lead to new expressions for the differential cross section. Therefore it is the aim of the present paper to derive the rotational state-to-state photoionization cross section for diatomic molecules, with the spin polarization of the electrons taken into account. We are looking for the probability of transition from an initial rotational level J'' of the neutral molecule to a final rotational level J_c of the ion when the photoelectron is ejected with momentum $\mathbf{k}$ and spin $\mathbf{s}$. We derive cross sections corresponding to two coupling schemes between angular momenta mentioned above. One is the transferred momentum (j_t) coupling scheme[11-13] and the other is the final-state (ion-plus-electron) angular momentum (J) coupling scheme.[16,17] An advantage of the first scheme is linked with the appearance of an incoherent sum in j_t and with easy introduction of a simple rotational factor. The second scheme, though leading to a more complicated formula, is convenient when studying autoionization resonances since a single term, corresponding to the total angular momentum J of the resonant state, gives dominant contribution to the cross section. The use of wave functions of definite parity in the initial and final states permits the writing of the transition moment and of the cross section in a form containing a selection-rule factor. By inspection of this simple factor it is possible to determine which transitions are allowed and contribute to the cross section. A similar selection-rule factor has been introduced by Dixit and McKoy[20] and Fredin *et al.*[21] in the context of multiphoton work. Variants of this selection rule have been derived by many other authors.

The equations obtained here are applicable also to the $n+1$ resonant multiphoton process. The preparation of the intermediate state by an n-photon excitation is ignored and one considers explicitly only the last, one-photon, ionization process.

The paper is organized as follows: In Sec. II we present the expression for the final- and initial-state wave functions with definite parity and for the corresponding transition moment. We also briefly discuss the selection rules for the transition moment and the cross section. In Sec. III we derive the rotational state-to-state cross section in the two coupling schemes discussed above and also average over the initial rotational states corresponding to a given temperature and sum over the final rotational states to obtain the photoabsorption spectrum. The theoretical photoabsorption cross sections can then be compared to the experimental spectra of Huth *et al.*[2] and Hart and Hepburn.[3] In Sec. IV we consider the example of photoionization of the HI molecule and give explicit formulas for the total cross section and $\bar{P}$ parameter in the case of $\Omega_c=\frac{3}{2}$ final ionic state with the l of the continuum electron restricted to 0,1,2. They can be directly used by experimentalists in the evaluation of the above-mentioned parameters. Section V is a conclusion.

II. FINAL-STATE WAVE FUNCTION AND TRANSITION MOMENT

We will consider a molecular photoionization in the nonrelativistic photon energy region where the electric-dipole approximation is valid. The radiation field is assumed to be so weak that only one-photon processes take place. Vibrational excitations of molecules are not considered here explicitly though all equations are written in a form which enables one to include them easily.

In our derivation we use two coordinate systems. One is the molecular coordinate system or molecule-fixed frame (primed coordinates and symbols) with the z' axis directed along the internuclear axis. The other one is the laboratory coordinate system or space-fixed frame (unprimed coordinates and symbols), with the vector $\mathbf{q}$ defining the laboratory z axis. This vector is directed along polarization vector $\mathbf{e}$ for the linearly polarized light or along the direction of light propagation for circularly polarized and unpolarized light. We present in Fig. 1

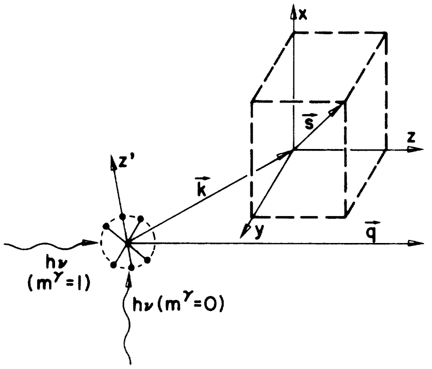

FIG. 1. Laboratory and molecular coordinate systems. The vector $\mathbf{q}$ defines the z axis of the laboratory coordinate system. It corresponds to the $\mathbf{e}$ vector for linearly polarized light or to the vector of photon momentum for circularly polarized light. The unit vectors $\mathbf{k}/|\mathbf{k}|$ and $\mathbf{s}/|\mathbf{s}|$ (to simplify the figure we use unnormalized vectors) are directed along the photoelectron momentum and spin, respectively. The z' axis is parallel to the internuclear axis.

these coordinate systems and the vectors appearing in the photoionization process. Latin and Greek letters correspond to the laboratory and molecular projections, respectively, the only exception being for the photoelectron spin with projections μ and σ corresponding to the space-fixed and molecule-fixed frames. The projections on the molecule-fixed frame are usually signed projections. We also introduce unsigned projections which are labeled with an overbar (e.g., $\bar{\Omega}$).

We will use lowercase symbols for the photoelectron wave function and quantum numbers, uppercase symbols with subscript c for the ion, and uppercase symbols without subscript for the ion-plus-electron system. We also use the spectroscopic notation for the initial states (i.e., Ω'', S'', etc.).

Throughout this paper we will use the atomic units $\hbar = m = e = 1$ for all the observables including the energy. The only exception is for the cross section which is expressed in cm^2.

A. Final-state wave function

The final-state wave function is an antisymmetrized product of an electron and an ion wave functions. Before considering this product, let us discuss first the wave function of the continuum electron in the laboratory frame with the ingoing normalization appropriate for photoionization:[22,23]

$$\psi_{s\mu}^{(-)}(\mathbf{k},\mathbf{r}) = \left[\frac{2}{\pi k}\right]^{1/2} \frac{1}{2ir} \sum_{l,m} \left[\sum_{l'} Y_{l'm}(\hat{\mathbf{r}})(e^{i\theta_{l'}}\delta_{l'l} - e^{-i\theta_{l'}} S_{l'l}^{m*})\right] i^l e^{-i\eta_l} Y_{lm}^*(\hat{\mathbf{k}}) |s\mu\rangle \ . \tag{1}$$

Here $[2/(\pi k)]^{1/2}$ is a factor normalizing the continuum wave function to the energy, $\mathbf{r}$ and $\mathbf{k}$ are the position and momentum vectors of the electron, and s is its spin (Fig. 1). The wave function (1) is expanded in spherical harmonics Y_{lm} in the space-fixed frame. The expression in small parentheses in (1) is the radial wave function of the electron, $S_{l'l}^{m}$ being the scattering amplitude in space-fixed frame. The spin-wave function is $|s\mu\rangle$ with μ being the projection of spin in this frame. θ_l is equal to $kr - (l\pi/2) - (Z/k)\ln(2kr) + \eta_l$ where $-(Z/k)\ln(2kr) + \eta_l$ is the Coulomb phase shift.[23,10] The corresponding function in the molecular frame of reference, where numerical calculations are usually performed, is $\varphi_{l\lambda\sigma}^{(-)}$ and is related to $\psi_{s\mu}^{(-)}$ by

$$\psi_{s\mu}^{(-)}(\mathbf{k},\mathbf{r}) = \sum_{\substack{l,\lambda \\ \sigma}} \varphi_{l\lambda\sigma}^{(-)}(k,\mathbf{r}') a_{l\lambda}^{s\sigma\mu}(\hat{\mathbf{k}},\hat{\mathbf{R}}) \ , \tag{2}$$

where

$$\varphi_{l\lambda\sigma}^{(-)}(k,\mathbf{r}') = \left[\frac{2}{\pi k}\right]^{1/2} \frac{1}{2ir} i^l e^{-i\eta_l} \sum_{l'} Y_{l'\lambda}(\hat{\mathbf{r}}')(e^{i\theta_{l'}}\delta_{l'l} - e^{-i\theta_{l'}} S_{l'l}^{\lambda*}) |s\sigma\rangle \tag{3}$$

and λ and σ are the projections of orbital angular momentum and spin in the molecular frame. The matrix $S_{l'l}^{\lambda}$ is the scattering matrix in the molecular frame. The symbol $\hat{\mathbf{R}}$ represents the three Euler angles relating the molecular frame to the laboratory one.

The transformation between these two frames[23,10,24] defines the coefficients $a_{l\lambda}^{s\sigma\mu}(\hat{\mathbf{k}},\hat{\mathbf{R}})$ of Eq. (2):

$$a_{l\lambda}^{s\sigma\mu}(\hat{\mathbf{k}},\hat{\mathbf{R}}) = \left[\sum_m Y_{lm}^*(\hat{\mathbf{k}}) \mathcal{D}_{\lambda m}^{(l)}(\hat{\mathbf{R}})\right] \mathcal{D}_{\sigma\mu}^{(s)}(\hat{\mathbf{R}}) \ . \tag{4}$$

Here $\mathcal{D}_{\lambda m}^{(l)}(\hat{\mathbf{R}})$ are rotational matrices in the Edmonds[24] notation.

It is obvious that the expressions (1)–(3) above are valid only asymptotically, i.e., far from the ionic core. The relations between these forms and expressions valid close to the ionic core are given in Eqs. (7) below.

The ion emerges from the photoionization process with total and spin angular momenta J_c and S_c, respectively. The projections of these momenta, and of orbital angular momentum in molecular frame, are Ω_c, Σ_c, and Λ_c. The projection of total angular momentum J_c in the laboratory frame is M_c. For simplicity, we use the notation $|\Lambda_c \Sigma_c \Omega_c\rangle$ for the electronic wave function of the ion. Obviously, this function depends parametrically on the internuclear distance. The corresponding rotational wave function is proportional to the rotational matrix $\mathcal{D}_{\Omega_c M_c}^{(J_c)}(\hat{\mathbf{R}})$. Instead of using a set of basis functions of the ion having either positive or negative projection Ω_c, we use linear combinations of these two functions which are properly symmetrized eigenfunctions of the total Hamiltonian.[25] The two possible linear combinations are called e and f states and have, following the notation of Chang and Fano,[26] parity factor η_c equal to $+1$ or -1, respectively.

We can now introduce the wave function of the complete system. Using (2), and the above considerations concerning the ionic state, this wave functions reads (see also Refs. 19 and 26):

$$\Psi^{J_c\eta_c}_{C\bar{\Omega}_c M_c\mu}(\mathbf{R},\mathbf{k},\mathbf{r})=\frac{1}{\sqrt{2}}[|\Lambda_c\Sigma_c\Omega_c\rangle\mathcal{D}^{(J_c)}_{\Omega_c M_c}(\hat{\mathbf{R}})+\eta_c(-1)^{1/2-S_c}|-\Lambda_c-\Sigma_c-\Omega_c\rangle\mathcal{D}^{(J_c)}_{-\Omega_c M_c}(\hat{\mathbf{R}})]\left[\frac{[J_c]}{8\pi^2}\right]^{1/2}\psi^{(-)}_{s\mu}(\mathbf{k},\mathbf{r})\ . \tag{5}$$

In (5) we have explicitly written only the coordinate of the continuum electron $\mathbf{r}$, omitting coordinates of the other electrons. We also use the abbreviation $C\equiv(n_c\Lambda_c\Sigma_c;S_c)$ where n_c represents all the nonexplicit quantum numbers. We can rewrite (5) in terms of a sum of eigenfunctions of the total angular momentum J of the electron-plus-ion system:

$$\Psi^{J_c\eta_c}_{C\bar{\Omega}_c M_c\mu}(\mathbf{R},\mathbf{k},\mathbf{r})=\sum_{\substack{J,j\\ l}}\sum_{\substack{m,m_j,\\ M}}[j,J]^{1/2}(-1)^{M_c+1/2}Y^*_{lm}(\hat{\mathbf{k}})\begin{bmatrix} l & s & j\\ m & \mu & -m_j\end{bmatrix}\begin{bmatrix} j & J_c & J\\ m_j & M_c & -M\end{bmatrix}\Psi^{J_c\eta_c,lj;J}_{C\bar{\Omega}_c;M}(\mathbf{R},k,\mathbf{r}')\ , \tag{6a}$$

where the eigenfunction of J, appearing in the right-hand side of (6a), has the following expression:

$$\begin{aligned}\Psi^{J_c\eta_c,lj;J}_{C\bar{\Omega}_c;M}(\mathbf{R},k,\mathbf{r}')=\sum_{\substack{\sigma,\omega\\ \lambda,\Omega}}&\frac{(-1)^{-\Omega_c-1/2}}{\sqrt{2}}[J,j]^{1/2}\begin{bmatrix} l & s & j\\ \lambda & \sigma & -\omega\end{bmatrix}\begin{bmatrix} j & J_c & J\\ \omega & \Omega_c & -\Omega\end{bmatrix}\\ &\times[|\Lambda_c\Sigma_c\Omega_c\rangle\varphi^{(-)}_{l\lambda\sigma}(k,\mathbf{r}')\mathcal{D}^{J}_{\Omega M}(\hat{\mathbf{R}})+\eta_c(-1)^{-S_c-s}(-1)^{l+s+J_c-J}\\ &\times|-\Lambda_c-\Sigma_c-\Omega_c\rangle\varphi^{(-)}_{l-\lambda-\sigma}(k,\mathbf{r}')\mathcal{D}^{(J)}_{-\Omega M}(\hat{\mathbf{R}})]\left[\frac{[J_c]}{8\pi^2}\right]^{1/2}\ .\end{aligned} \tag{6b}$$

Here j is the total angular momentum of the excited electron with m_j and ω being its projections in laboratory and molecular frames, respectively. In the last three equations we have used the notation $[J]=2J+1$ and also $[j,J]=(2j+1)(2J+1)$. Equation (6) corresponds to the Hund coupling case (c) between the ion and the electron. The explicit reference to this coupling case is essential here as it is directly related to the observation of the spin polarization of the photoelectron appearing through the spin-orbit interaction. The matrix elements of this interaction, and of the transition moment, take their main contribution in a region of space where the electron and the ion are close to each other (internal region). In this region we have to enforce the antisymmetry of the wave function and consequently the function (6b), valid in the external region, is inappropriate. We define an internal region wave function $\chi^{JM\eta,l\lambda\sigma}_{\Lambda\Sigma\Omega,\bar{\Omega}_c}$ and connect it to the external region wave function (6b) in the following way:

$$\begin{aligned}&\Psi^{J_c\eta_c lj;J}_{C\bar{\Omega}_c;M}(\mathbf{R},k,\mathbf{r}')\\ &\qquad=\sum_{\substack{\sigma\\ \lambda,\Omega\\ \eta}}\chi^{JM\eta,l\lambda\sigma}_{\Lambda\Sigma\Omega,\bar{\Omega}_c}(\mathbf{R},k,\mathbf{r}')U^{J_cS_c,lsj;J\eta\eta_c}_{\bar{\Omega}_c\lambda\sigma,\Omega}\ .\end{aligned} \tag{7a}$$

The wave function $\chi^{JM\eta,l\lambda\sigma}_{\Lambda\Sigma\Omega\bar{\Omega}_c}$ is written as a sum of products of electronic wave functions $\theta^{l\lambda\sigma}_{\Lambda_c\Sigma_c\Omega_c}(k,\mathbf{r}',R)$ and rotational functions $\mathcal{D}^{J}_{\Omega M}(\hat{\mathbf{R}})$:

$$\chi^{JM\eta,l\lambda\sigma}_{\Lambda\Sigma\Omega,\bar{\Omega}_c}=\frac{(-1)^{\Omega_c+1/2}}{\sqrt{2}}[\theta^{l\lambda\sigma}_{\Lambda_c\Sigma_c\Omega_c}(k,\mathbf{r}',R)\mathcal{D}^{(J)}_{\Omega M}(\hat{\mathbf{R}})+\eta(-1)^{1}\theta^{l-\lambda-\sigma}_{-\Lambda_c-\Sigma_c-\Omega_c}(k,\mathbf{r}',R)\mathcal{D}^{(J)}_{-\Omega M}(\hat{\mathbf{R}})]\left[\frac{[J]}{8\pi^2}\right]^{1/2}, \tag{7b}$$

$$\chi^{JM\eta,l\lambda\sigma}_{\Lambda\Sigma\Omega,\bar{\Omega}'_c}=\frac{(-1)^{\Omega'_c+1/2}}{\sqrt{2}}[\theta^{l\lambda\sigma}_{\Lambda_c-\Sigma_c\Omega'_c}(k,\mathbf{r}',R)\mathcal{D}^{(J)}_{\Omega M}(\hat{\mathbf{R}})+\eta(-1)^{1}\theta^{l-\lambda-\sigma}_{-\Lambda_c\Sigma_c-\Omega'_c}(k,\mathbf{r}',R)\mathcal{D}^{(J)}_{-\Omega M}(\hat{\mathbf{R}})]\left[\frac{[J]}{8\pi^2}\right]^{1/2}\ . \tag{7c}$$

In the particular case of a Π ionic state the wave functions (7b) and (7c) correspond to $\Omega_c=\frac{3}{2}$ and $\frac{1}{2}$ projections, respectively. The electronic wave function $\theta^{l\lambda\sigma}_{\Lambda_c\Sigma_c\Omega_c}$ is an antisymmetric product of the ionic core wave function $|\Lambda_c\Sigma_c\Omega_c\rangle$ ($^2\Pi$ state in our case) and the continuum electron wave function $\varphi^{(-)}_{l\lambda\sigma}$:

$$\theta^{l\lambda\sigma}_{\Lambda_c\Sigma_c\Omega_c}=||\Lambda_c\Sigma_c\Omega_c\rangle\varphi^{(-)}_{l\lambda\sigma}|\ .$$

In fact, $\theta^{l\lambda\sigma}_{\Lambda_c\Sigma_c\Omega_c}$ is a linear combination of triplet and singlet states[9] each constructed from at least one Slater determinant.

The coefficients U of the frame transformation between the internal (6b) and asymptotic wave functions (7a) are obtained requiring the continuity between these two functions:

$$U^{J_cS_c,lsj;J\eta\eta_c}_{\bar{\Omega}_c\lambda\sigma\Omega}=\sum_{\omega}\begin{bmatrix} l & s & j\\ \lambda & \sigma & -\omega\end{bmatrix}\begin{bmatrix} j & J_c & J\\ \omega & \Omega_c & -\Omega\end{bmatrix}[J_c,j]^{1/2}\frac{1+\eta(-1)^{1}\eta_c(-1)^{-S_c-s}(-1)^{l+s+J_c-J}}{2}\ . \tag{7d}$$

B. Transition moment

Consider now the transition moment corresponding to the excitation from an initial state with the wave function $\Psi^{J''\eta''}_{\bar{\Omega}''M''}$ by the dipole transition operator $\hat{T}_{m^\gamma}$ to a final continuum state with the wave function $\Psi^{J_c\eta_c}_{C\Omega_c M_c\mu}(\mathbf{R},\mathbf{k},\mathbf{r})$. The final-state N-electron wave function has been defined in Sec. II A [Eqs. (5)–(7)]. Similarly, the initial-state wave function reads

$$\Psi^{J''\eta''}_{n''\bar{\Omega}''M''}=\sum_{\Omega''}{}' \eta_{\bar{\Omega}'',\Omega''}\Psi^{J''}_{n''\Omega''M''}$$

$$=\Psi^{J''}_{n''\Omega''M''}+\eta''(-1)^{-S''}\Psi^{J''}_{n''-\Omega''M''}\ , \tag{8a}$$

where

$$\begin{aligned}\eta_{\bar{\Omega}'',\Omega''}&=1 \quad \text{when } \Omega''=\bar{\Omega}''\ ,\\ \eta_{\bar{\Omega}'',\Omega''}&=\eta''(-1)^{-S''} \quad \text{when } \Omega''=-\bar{\Omega}''\ ,\end{aligned} \tag{8b}$$

and

$$\Psi^{J''}_{n''\Omega''M''}=\left[\frac{[J'']}{16\pi^2}\right]^{1/2}|n''\Omega''\rangle\mathcal{D}^{(J'')}_{\Omega''M''}(\hat{\mathbf{R}})\ , \tag{8c}$$

where the quantum numbers of the initial state are the total angular momentum J'' with its projection in molecular and laboratory frames Ω'' and M'', respectively, the parity η'', and the total spin S''. The symbols n'' and $\sum'_{\Omega''}$ represent all other quantum numbers not specified explicitly and a sum over signed projections Ω'', conserving a constant module $\bar{\Omega}''=$const. Using (7) and (8) the transition moment corresponding to a total angular momentum J can be written as

$$\begin{aligned}\langle\Psi^{J_c\eta_c,lj;J}_{C\bar{\Omega}_cM_c\mu}|\hat{T}_{m^\gamma}|\psi^{J''\eta''}_{n''\bar{\Omega}''M''}\rangle_{\mathbf{r},\mathbf{R}}=&\sum_{\substack{\lambda,\sigma\\ \Omega}}\frac{(-1)^{\Omega_c+1/2}}{2}\sum_{\lambda^\gamma}\sum_{\Omega''}{}'\langle\theta^{l\lambda\sigma}_{\Lambda_c\Sigma_c\Omega_c}|\hat{T}_{\lambda^\gamma}|n''\Omega''\rangle_{\mathbf{r},R}\,\eta_{\bar{\Omega}'',\Omega''}\\ &\times\left[\int\mathcal{D}^{(J)*}_{\Omega M}(\hat{\mathbf{R}})\mathcal{D}^{(1)}_{\lambda^\gamma m^\gamma}(\hat{\mathbf{R}})\mathcal{D}^{(J'')}_{\Omega''M''}(\hat{\mathbf{R}})d\hat{\mathbf{R}}\right.\\ &\left.+\eta''(-1)^{S''}\eta(-1)^{1}\int\mathcal{D}^{(J)*}_{\Omega M}(\hat{\mathbf{R}})\mathcal{D}^{(1)}_{\lambda^\gamma m^\gamma}(\hat{\mathbf{R}})\times\mathcal{D}^{(J'')}_{-\Omega''M''}(\hat{\mathbf{R}})d\hat{\mathbf{R}}\right]\\ &\times\frac{[J'',J]^{1/2}}{8\pi^2}U^{J_cS_c,ls;J\eta\eta_c}_{\Omega_c\lambda\sigma,\Omega}\ ,\end{aligned} \tag{9}$$

where $\hat{T}_{\lambda^\gamma}=(4\pi/3)^{1/2}r'Y_{1\lambda^\gamma}(\hat{\mathbf{r}}')$ is the transition moment operator in the molecular frame with λ^γ being the projection of photon angular momentum in this frame. The transition moment in the molecular frame satisfies the following conditions:

$$\langle\theta^{l\lambda\sigma}_{\Lambda_c\Sigma_c\Omega_c}|\hat{T}_{\lambda^\gamma}|n''\pm\Omega''\rangle$$

$$=\langle\theta^{l-\lambda-\sigma}_{-\Lambda_c-\Sigma_c-\Omega_c}|\hat{T}_{-\lambda^\gamma}|n''\mp\Omega''\rangle\ ,$$

which was used in the derivation of (9). Note that when $\Omega''\neq0$ and $\Omega_c\neq0$ each expression in (9), corresponding to a given value of λ, σ, Ω, and λ^γ, contains four terms as in the similar expression derived by Dixit and McKoy.[20] If, in Eq. (9), we assume dipole transitions (i.e., $\lambda^\gamma=0,\pm1$), then only two terms, but not always the same, are different from zero. Performing analytically the integration over $\hat{R}$, and using the expressions (7a), (7d), and (6), we can write the transition moment as a sum of transition moments (9) corresponding to different total angular momentum J of the final-state wave function (5):

$$\begin{aligned}&\langle\Psi^{J_c\eta_c}_{C\bar{\Omega}_cM_c\mu}(\mathbf{R},\mathbf{k},\mathbf{r})|\hat{T}_{m^\gamma}|\Psi^{J''\eta''}_{n''\bar{\Omega}''M''}\rangle_{\mathbf{r},\mathbf{R}}\\ &=\sum_{\substack{J,j\\ l}}\sum_{\substack{M,m_j\\ m}}[J'',j,J]^{1/2}(-1)^{M_c+1/2-m^\gamma-M''}Y^*_{lm}(\hat{\mathbf{k}})\begin{pmatrix}l & s & j\\ m & \mu & -m_j\end{pmatrix}\begin{pmatrix}j & J_c & J\\ m_j & M_c & -M\end{pmatrix}\\ &\quad\times\begin{pmatrix}J & 1 & J''\\ -M & m^\gamma & M''\end{pmatrix}\sum_{\Omega''}{}'\sum_{\Omega,\lambda^\gamma}(-1)^{\Omega_c+1/2+\Omega''}[J_c]^{1/2}\langle J_c\bar{\Omega}_c,lj|T(J)|\Omega''\rangle\\ &\quad\times\begin{pmatrix}J & 1 & J''\\ -\Omega & \lambda^\gamma & \Omega''\end{pmatrix}\{\tfrac{1}{2}[1+\eta''\eta_c(-1)^{-S_c-s-S''}(-1)^{l+s+J_c+1+J''}]\}\ ,\end{aligned} \tag{10a}$$

where

$$\langle J_c\bar{\Omega}_c,lj|T(J)|\Omega''\rangle=[j,J]^{1/2}\sum_{\substack{\lambda,\sigma\\ \omega}}(-1)^{\lambda^\gamma}\eta_{\bar{\Omega}'',\Omega''}t^{\bar{\Omega}_c,l\lambda}_{n''\Omega''}(\varepsilon)\begin{pmatrix}l & s & j\\ \lambda & \sigma & -\omega\end{pmatrix}\begin{pmatrix}j & J_c & J\\ \omega & \Omega_c & -\Omega\end{pmatrix} \tag{10b}$$

and

$$t_{n''\Omega''}^{\bar{\Omega}_c,l\lambda}(\varepsilon)=\langle \theta^{l\lambda\sigma}_{\Lambda_c\Sigma_c\bar{\Omega}_c}|\hat{T}_{\lambda^\gamma}|n''\Omega''\rangle \ . \tag{10c}$$

In (10) ε is the kinetic energy of the electron. The integral in Eq. (10c) is over the coordinates of all the electrons including $\mathbf{r}$ of the excited one. It can be calculated in a one-configuration representation or in the configuration-interaction representation using the method of Ref. 27 based on the Lowdin first-order density matrix.

The above expression for the transition moment is appropriate for the analysis of resonances since the total angular momentum J of the final state is explicitly defined. This is so as a resonance corresponds to a discrete state having a single J. It interacts only with one term in the sum (selection rule $\Delta J=0$) of several continuum states taken into account in Eq. (10a). Consequently at resonance only one term of (10) contributes to the cross section. In the following we will call this form the "resonance form." The expression in the last set of curly braces of (10a) is called the "selection-rule factor." This factor is independent of J of the final electron-plus-ion state and of projections. As will be seen below, it contains very simple information about the selection rules for a transition.

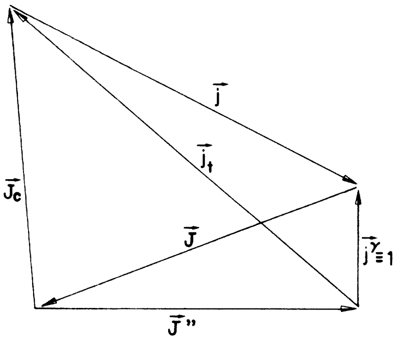

FIG. 2. The vector diagram corresponding to two coupling schemes for the angular momenta of the molecular photoionization process including rotation. The vectors corresponding to observable quantities are $\mathbf{J}$, $\mathbf{j}^\gamma$, and $\mathbf{J}_c$, which are the initial state, photon, and final ionic state angular momenta, respectively. The other three angular momenta $\mathbf{j}$, $\mathbf{j}_t$, and $\mathbf{J}$ are defined by the space orientation of $\mathbf{J}$, $\mathbf{j}^\gamma$, and $\mathbf{J}_c$.

The expression (10) can also be written in a different form similar to the one introduced by Buckingham, Orr, and Sichel[11] or Fano and Dill.[13] This form can be obtained from (10) using a transformation to 6-j symbols [see, e.g., Rotenberg *et al.*,[28] Eqs. (2.19) and (2.6)]. It is written in terms of transferred angular momentum which is defined as $\mathbf{j}_t=\mathbf{J}_c-\mathbf{J}''=\mathbf{j}^\gamma-\mathbf{j}$, where $\mathbf{j}^\gamma\equiv 1$ is the angular momentum of the photon. An equation equivalent to (10a) in this formulation reads

$$\begin{aligned}\langle \Psi^{J_c\eta_c}_{C\bar{\Omega}_cM_c\mu}(\mathbf{R},\mathbf{k},\mathbf{r})|\hat{T}_{m^\gamma}|\Psi^{J''\eta''}_{n''\bar{\Omega}''M''}\rangle_{\mathbf{r},\mathbf{R}}&\\ =\sum_{\substack{j_t,j\\ l}}\sum_{\substack{m_{j_t},m_j\\ m}}[J'',j,j_t]^{1/2}(-1)^{M_c-m_{j_t}}Y^*_{lm}(\hat{\mathbf{k}})&\begin{bmatrix} l & s & j\\ m & \mu & -m_j\end{bmatrix}\begin{bmatrix} j & 1 & j_t\\ m_j & -m^\gamma & m_{j_t}\end{bmatrix}\\ \times\begin{bmatrix} J'' & J_c & j_t\\ -M'' & M_c & -m_{j_t}\end{bmatrix}&\sum_{\Omega''}{}'(-1)^{-\Omega''}[J_c]^{1/2}\begin{bmatrix} J'' & J_c & j_t\\ -\Omega'' & \Omega_c & \Omega''-\Omega_c\end{bmatrix}\\ &\times\{\tfrac{1}{2}[1+\eta''\eta_c(-1)^{-s-S_c-S''}(-1)^{l+s+J_c+1+J''}]\}\langle\bar{\Omega}_c,lj|T(j_t)|\Omega''\rangle\ ,\end{aligned}\tag{11a}$$

where the last factor in (11a) has the following expression:

$$\langle\bar{\Omega}_c,lj|T(j_t)|\Omega''\rangle=[j,j_t]^{1/2}\sum_{\substack{\lambda,\sigma\\ \omega,\lambda^\gamma}}\eta_{\bar{\Omega}'',\Omega''}t^{\bar{\Omega}_c,l\lambda}_{n''\Omega''}(\varepsilon)\begin{bmatrix} l & s & j\\ \lambda & \sigma & -\omega\end{bmatrix}\begin{bmatrix} j & 1 & j_t\\ \omega & -\lambda^\gamma & \Omega_c-\Omega''\end{bmatrix}\ . \tag{11b}$$

We call this form of the transition moment [Eq. (11)] the "scattering form" as the momentum transferred during the collision of the excited electron with the ionic core is well defined. Using this formulation, we obtain a much simpler expression (see Sec. III) for the cross section and polarization parameters with incoherent sum over the transferred momentum j_t.

Finally, to get some more insight in the meaning of these two coupling schemes, we have drawn, in Fig. 2, a vector diagram of momenta. (See similar diagram in Ref. 14). The vectors corresponding to observable quantities are $\mathbf{J}''$, $\mathbf{j}^\gamma$, and $\mathbf{J}_c$. They can take different orientations in space, each orientation corresponding to a term in the summations of Eqs. (10) and (11). Given their orientation, these vectors completely define the other three vectors $\mathbf{j}$, $\mathbf{J}$, and $\mathbf{j}_t$. The vectors $\mathbf{J}$ and $\mathbf{j}_t$ do not correspond to some observable quantities, but they are useful for the interpretation of the photoionization process.

C. Selection rules for transition

The analysis of expression (10) and (11) in terms of allowed quantum numbers and projections will give us the selection rules for the photoionization process. The last 3-*j* symbol of (10a) and (11a) gives two restrictions, respectively:

$$\begin{aligned} &\Omega \mp \bar{\Omega}'' = \lambda^{\gamma} = 0, \pm 1 \quad \text{and} \quad |J''-1| \le J \le J''+1 \ , \\ &\Omega_c \mp \bar{\Omega}'' = \lambda_{j_t} \quad \text{and} \quad |J''-j_t| \le J_c \le J''+j_t \ . \end{aligned} \tag{12}$$

The first line in (12) is the standard selection rule for the discrete spectrum, whereas the second line in (12) restricts the possible rotational states of the ion. The selection-rule factor, appearing between curly braces in (10) and (11), gives a supplementary selection rule:

$$J_c + J'' + s + l + (1-\eta_c)/2 + (1-\eta'')/2 - s - S_c - S'' = \text{odd} \ . \tag{13}$$

This selection rule is identical to the one derived by Dixit and McKoy[20] in the framework of their multiphoton work. It is analogous to those derived by Raoult, Jungen, and Dill,[15] Dixit *et al.*,[29] and Fredin *et al.*[21] without explicit consideration of the spin. We can obtain a simple proof of their selection rules by replacing *j* by *l* in the above equations, suppressing the 3*j* coefficient

$$\begin{pmatrix} l & s & j \\ \lambda & \sigma & -\omega \end{pmatrix}$$

and eliminating the spin from Eq. (13). For $\eta_c = 1$ we therefore obtain $\Delta J + l = \text{odd}$ of Dixit *et al.*,[29] or in the case of $l = 1$, $\Delta J = \text{even}$ of Raoult, Jungen, and Dill.[15] Finally the Fredin *et al.*[21] selection-rule factor is obtained by replacing their l' of the initial state by $l+1$ of the final state and also N' and N^+ by J'' and J_c, respectively.

The cross section, derived in Sec. III, is proportional to a product of two transition moments and therefore contains a product of two selection-rule factors which, when calculated explicitly, gives

$$\mathcal{S}^{J_c S_c \eta_c}_{J'' S'' \eta''}(l_1, l_2) = \tfrac{1}{2}\left[\delta_{l_1+l_2,2n} + \eta_{l_1 l_2}\eta''\eta_c(-1)^{-s-S_c-S''} \times (-1)^{s+J_c+1+J''}\right] , \tag{14a}$$

where $\delta_{l_1+l_2,2n}$ is the Kronecker symbol and everything else has already been defined except for

$$\eta_{l_1 l_2} = \tfrac{1}{2}[(-1)^{l_1} + (-1)^{l_2}] \ . \tag{14b}$$

This factor is $+1$ or -1 when both l_1 and l_2 are even or odd and zero otherwise. It appears from (14) that $\mathcal{S}^{J_c S_c \eta_c}_{J'' S'' \eta''}(l_1, l_2)$, and consequently the cross section, is different from zero only when l_1 and l_2 are of the same parity. The condition $l_1 + l_2 = \text{even}$ is in fact the same as the condition $l_1 + l_2 + L = \text{even}$ and $L = \text{even}$ obtained from a 3-*j* symbol appearing in Eqs. (19b) and (20c) below.

III. ROTATIONAL STATE TO STATE DIFFERENTIAL CROSS SECTION

The square of the dipole matrix element, defined in the preceding section [Eqs. (10) and (11)], gives the probability of the ejection of an electron in the direction **k** with the spin oriented along the *z* axis of the space-fixed frame. The angular distribution of photoelectrons with defined spin polarization (ADSP), or the differential photoionization cross section for ejection of an electron in the direction **k**, with its spin oriented along another direction **s** (see Fig. 1), is given by (Cherepkov,[7] Raseev, Keller, and Lefebvre,[10] and Huang[30])

$$\begin{aligned} {}^{m^{\gamma}}I^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}'' J'' \eta''}(\mathbf{k},\mathbf{s}) = \frac{N_E}{[J'']} \sum_{\mu_1,\mu_2} \sum_{M'',M_c} &\langle \Psi^{J''\eta''}_{n''\bar{\Omega}''M''} | \hat{T}_{m^{\gamma}} | \Psi^{J_c\eta_c}_{C\bar{\Omega}_c M_c \mu_1}(\mathbf{R},\mathbf{k},\mathbf{r}) \rangle \tfrac{1}{2}[1 + (\mathbf{s}/|\mathbf{s}|)\boldsymbol{\sigma}]_{\mu_1\mu_2} \\ &\times \langle \Psi^{J_c\eta_c}_{C\bar{\Omega}_c M_c \mu_2}(\mathbf{R},\mathbf{k},\mathbf{r}) | \hat{T}_{m^{\gamma}} | \Psi^{J''\eta''}_{n''\bar{\Omega}''M''} \rangle \ . \end{aligned} \tag{15}$$

The coefficient $N_E = (4\pi^2 \alpha a_0^2 E_{\text{ph}})$ is a function of the photon energy E_{ph} only. This photon energy is, in fact, the energy difference between final and initial states. It should be expressed in the same units as the energy normalization of the final-state wave function (1). Note that $\alpha = 137.037$ is the dimensionless fine-structure constant, and a_0 is the Bohr radius. The operator $\frac{1}{2}[1 + (\mathbf{s}/|\mathbf{s}|)\boldsymbol{\sigma}]$, with $\boldsymbol{\sigma}$ being the Pauli matrix vector, is the operator projecting spin on the $\mathbf{s}/|\mathbf{s}|$ direction. It can be presented in the following explicit form:[31]

$$\tfrac{1}{2}[1 + (\mathbf{s}/|\mathbf{s}|)\boldsymbol{\sigma}]_{\mu_1\mu_2} = \sum_{S,M_s} (-1)^{1/2-\mu_2} \sqrt{2\pi}\, Y_{S-M_s}(\hat{\mathbf{s}}) \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S \\ \mu_1 & -\mu_2 & -M_s \end{pmatrix} . \tag{16}$$

Here we have coupled two spin functions in the usual way.[24]

The laboratory coordinate system and the different vectors appearing in the photoionization process [see Eq. (15)] are drawn in Fig. 1 and were mentioned in the preceding section. Compared to photoionization without rotation, no supplementary vectors appear because in the gas phase we are averaging over the random orientation of the molecular frame.

Now, we obtain two workable expressions for ADSP, corresponding to two coupling schemes of the angular momenta involved. To this end we select one of the corresponding transition moments (10) or (11) and together with (16) introduce them in (15). Then we transform the product $Y_{l_1 m}(\hat{\mathbf{k}}) Y_{l_2 m}(\hat{\mathbf{k}})$ in a sum of spherical harmonics $Y_{LM_L}(\mathbf{k})$;[24,13] to obtain final expressions, we perform analytic summation over projections in the laboratory frame. The result is

$$ {}^{m^\gamma}I^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}(\mathbf{k},\mathbf{s})=\frac{\sqrt{3}}{2}\sigma^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}(\varepsilon)\sum_{\substack{K,L,S\\ M_L}}(-1)^{1+m^\gamma}\begin{pmatrix}1 & 1 & K\\ m^\gamma & -m^\gamma & 0\end{pmatrix}Y_{LM_L}(\hat{\mathbf{k}})Y_{S-M_L}(\hat{\mathbf{s}})C^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}(K,L,S,M_L,\varepsilon)\ , \tag{17}$$

where for $K=L=M_L=S=0$ the coefficient $C^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}(0,0,0,0,\varepsilon)$ is normalized to unity. The angular momenta L and S correspond to the coupling of angular momenta of the electron, whereas K is related to the angular momentum of the photon. The total cross section appearing in (17) reads

$$\sigma^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}(\varepsilon)=\frac{N_E}{3}B^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}(\varepsilon)\ . \tag{18}$$

We give below the particular form of $B^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}(\varepsilon)$ and $C^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}(K,L,S,M,\varepsilon)$ in the cases of the two coupling schemes.

(a) When we use the "resonance form" of the transition moment (10), the resulting expressions are written in terms of rotational quantum numbers J_1 and J_2 of the final state (ion plus electron):

$$B^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}(\varepsilon)=\frac{[J_c]}{[J'']}\sum_{\substack{l,j\\ J}}\sideset{}{'}\sum_{\substack{\Omega''\\ \tilde\Omega''}}\sum_{\substack{\sigma,\lambda^\gamma\\ \lambda,\Omega\\ \omega}}Q^{\Omega J,\Omega J}_{\Omega''\tilde\Omega'' J''}\mathcal{S}^{S_c J_c \eta_c}_{S'' J'' \eta''}(l,l)\langle J_c\bar\Omega_c,lj|T(J)|\Omega''\rangle\langle\tilde\Omega''|T(J)|\bar\Omega_c J_c,lj\rangle\ , \tag{19a}$$

where $\mathcal{S}^{S_c J_c \eta_c}_{S'' J'' \eta''}(l_1,l_2)$ is given by expression (14a) and

$$\begin{aligned}C^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}&(K,L,S,M_L,\varepsilon)\\ &=\sqrt{6}\frac{(-1)^K[K,J_c][L]^{1/2}}{[J'']B^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}(\varepsilon)}\sum_{\substack{J_1,j_1\\ l_1}}\sum_{\substack{J_2,j_2\\ l_2}}(-1)^{1+j_2+l_2+J_c+J''}[j_1,j_2,l_1,l_2]^{1/2}\begin{pmatrix}K & L & S\\ 0 & M_L & -M_L\end{pmatrix}\\ &\quad\times\begin{Bmatrix}j_1 & j_2 & K\\ l_1 & l_2 & L\\ \frac{1}{2} & \frac{1}{2} & S\end{Bmatrix}\begin{Bmatrix}1 & 1 & K\\ J_1 & J_2 & J''\end{Bmatrix}\begin{Bmatrix}J_1 & J_2 & K\\ j_1 & j_2 & J_c\end{Bmatrix}\begin{pmatrix}l_1 & l_2 & L\\ 0 & 0 & 0\end{pmatrix}\mathcal{S}^{S_c J_c \eta_c}_{S'' J'' \eta''}(l_1,l_2)\\ &\quad\times\sideset{}{'}\sum_{\substack{\Omega''\\ \tilde\Omega''}}\sum_{\substack{\lambda_1^\gamma\\ \Omega_1}}\sum_{\substack{\lambda_2^\gamma\\ \Omega_2}}Q^{\Omega_1 J_1,\Omega_2 J_2}_{\Omega''\tilde\Omega'' J''}\langle J_c\bar\Omega_c,l_1 j_1|T(J_1)|\Omega''\rangle\langle\tilde\Omega''|T(J_2)|J_c\bar\Omega_c,l_2 j_2\rangle\ ,\end{aligned} \tag{19b}$$

where the expression for $Q^{\Omega_1 J_1,\Omega_2 J_2}_{\Omega''\tilde\Omega'' J''}$ is

$$Q^{\Omega_1 J_1,\Omega_2 J_2}_{\Omega''\tilde\Omega'' J''}=[J''][J_1,J_2]^{1/2}\begin{pmatrix}J_1 & 1 & J''\\ -\Omega_1 & \lambda_1^\gamma & \Omega''\end{pmatrix}\begin{pmatrix}J_2 & 1 & J''\\ -\Omega_2 & \lambda_2^\gamma & \tilde\Omega''\end{pmatrix}\ . \tag{19c}$$

Note that, in (19a), we obtain a double summation over Ω'' and $\tilde\Omega''$, with the same convention for the sum symbol as in (8a), i.e., summation over signed projections and constant module ($\bar\Omega''=\bar{\tilde\Omega}''=\text{const}$).

(b) When we use the "scattering form" of the transition moment (11), the resulting expressions are written in terms of transferred momentum j_t:

$$B^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}(\varepsilon)=\frac{1}{[J'']}\sum_{j_t}\sideset{}{'}\sum_{\substack{\Omega''\\ \tilde\Omega''}}Q^{\bar\Omega_c J_c}_{\Omega''\tilde\Omega'' J''}(j_t)c^{\bar\Omega_c J_c \eta_c}_{\Omega''\tilde\Omega'' J'' \eta''}(0,0,0,j_t,\varepsilon)\ , \tag{20a}$$

$$C^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}(K,L,S,M_L,\varepsilon)=\sqrt{6}\frac{[K][L]^{1/2}}{[J'']B^{\bar\Omega_c J_c \eta_c}_{\bar\Omega'' J'' \eta''}(\varepsilon)}\begin{pmatrix}K & L & S\\ 0 & M_L & -M_L\end{pmatrix}\sum_{j_t}\sideset{}{'}\sum_{\substack{\Omega''\\ \tilde\Omega''}}Q^{\bar\Omega_c J_c}_{\Omega''\tilde\Omega'' J''}(j_t)c^{\bar\Omega_c J_c \eta_c}_{\Omega''\tilde\Omega'' J'' \eta''}(K,L,S,j_t,\varepsilon)\ , \tag{20b}$$

where

$$\begin{aligned}c^{\bar\Omega_c J_c \eta_c}_{\Omega''\tilde\Omega'' J'' \eta''}(K,L,S,j_t,\varepsilon)&=\sum_{\substack{j_1,j_2\\ l_1,l_2}}(-1)^{l_2+j_t+j_1+1}[j_1,j_2,l_1,l_2]^{1/2}\begin{Bmatrix}j_1 & j_2 & K\\ l_1 & l_2 & L\\ \frac{1}{2} & \frac{1}{2} & S\end{Bmatrix}\begin{Bmatrix}1 & 1 & K\\ j_1 & j_2 & j_t\end{Bmatrix}\\ &\quad\times\begin{pmatrix}l_1 & l_2 & L\\ 0 & 0 & 0\end{pmatrix}\mathcal{S}^{S_c J_c \eta_c}_{S'' J'' \eta''}(l_1,l_2)\langle\bar\Omega_c,l_1 j_1|T(j_t)|\Omega''\rangle\langle\tilde\Omega''|T(j_t)|\bar\Omega_c,l_2 j_2\rangle\end{aligned} \tag{20c}$$

and

$$Q^{\bar{\Omega}_c J_c}_{\Omega''\tilde{\Omega}''J''}(j_t)=[J'',J_c]\begin{pmatrix} J'' & j_t & J_c \\ -\Omega'' & \Omega''-\bar{\Omega}_c & \bar{\Omega}_c \end{pmatrix}\begin{pmatrix} J'' & j_t & J_c \\ -\tilde{\Omega}'' & \tilde{\Omega}''-\bar{\Omega}_c & \bar{\Omega}_c \end{pmatrix} . \tag{20d}$$

In the case of cross section, expressions (18) and (20a), the factor (20c) can be written in a very simple form:

$$c^{\bar{\Omega}_c J_c \eta_c}_{\Omega''\tilde{\Omega}''J''\eta''}(0,0,0,j_t,\varepsilon)=\sum_{l,j}\langle\bar{\Omega}_c,lj|T(j_t)|\Omega''\rangle\langle\tilde{\Omega}''|T(j_t)|\bar{\Omega}_c,lj\rangle\mathcal{S}^{S_c J_c \eta_c}_{S''J''\eta''}(l,l) . \tag{20e}$$

Obviously Eqs. (19) have a more complicated structure than Eqs. (20) because in (19) we have a coherent summation in terms of J_1 and J_2, whereas in (20) an incoherent summation over j_t occurs. The assignment and analysis of the P, Q, and R branches of a resonance using the "resonance form" is easier as each branch corresponds to only one term in the summations (19). The equivalent analysis using the "scattering form" is more complicated since it requires, for a description of a single branch, several terms in the expansion (20). Nevertheless, far from a resonance this scattering form permits us to analyze the spectrum in terms of momentum transferred between the ion and the electron during the "half collision" process.

A further comparison between these two forms concerns the so-called rotational factor $Q_{\Omega''\tilde{\Omega}''J''}$ [Eqs. (19c) and (20d)]. In the resonance-form expression for B [Eq. (19a)] the $\Omega^{\Omega J,\Omega j}_{\Omega''\tilde{\Omega}''J''}$ factor reduces, after summation over Ω'' and Ω, to rotational line strength factor of a discrete-discrete transition defined by Zare.[32] In the case of Ω'' and/or Ω equal o zero, it reduces to the well-known Hönl-London factor.[32,33] The scattering form of this factor [$Q^{\bar{\Omega}_c J_c}_{\Omega''\tilde{\Omega}''J''}$; Eq. (20d)] is similar to the discrete-discrete rotational line strength factor but it is written in terms of the rotational quantum number of the ion and the transferred momentum instead of final-state rotational and photon quantum numbers. As this factor is identical for all the polarization parameters, it can be called, after summation over projections, rotational line strength factor for photoionization. Note, finally, that this factor reduces to a square of 3-j symbols on cases when $\Omega''=0$ and/or $\Omega_c=0$ and we recover the result by Dill.[14]

When neglecting the electron spin, the scattering-form expressions (18), (20a), and (20e) for the cross section are the same as the formulas obtained by Fano[34] in the case of rotationally resolved photoionization of the H_2 molecule. Furthermore, if we neglect the parity (i.e., sum over η'' and η_c) we recover the general expressions of Buckingham, Orr, and Sichel[11] and Sichel.[12]

Usually, in photoelectron spectra states corresponding to different η'' of the neutral molecule or η_c of the ion (i.e., e,f states) lie energetically very close to each other and are consequently not resolved. In a discrete spectrum these states (neutral or ionic) correspond to two components of the Λ doubling.[32,33] Neglecting the Λ doubling in both states implies that in (19) and (20) we perform the summation over η'' and η_c. Then the selection-rule factor $\mathcal{S}^{S_c J_c \eta_c}_{S''J''\eta''}(l_1,l_2)$ [see Eqs. (19b) and (20c)] reduces to $\delta_{l_1,+l_2,2n}$ and the double summation over Ω'' and $\tilde{\Omega}''$ reduces to a simple summation. The condition $\delta_{l_1,+l_2,2n}$ is the same as the standard condition $\delta_{l_1+l_2+L,2n}$ and L even obtained by inspection of 3-j coefficients in (19b) and (20c) and we recover the expression for cross section corresponding to parity-undefined states. In the case of nondegenerate initial states, a further analysis reveals that if Λ doubling of the ion is resolved in heteronuclear molecules both components are populated by photoionization as any l is allowed by symmetry. For homonuclear molecules only one Λ-doubling component of the ion is populated by photoionization and we should obtain the same result in the case of resolved or unresolved Λ doubling.

Starting from (17) and using explicit formulas for the two spherical harmonics appearing in that equation, we can introduce the electron spin-polarization parameters as coefficients before all nonzero terms in the summations over K, L, S, and M_L. Each of these polarization parameters will correspond to a particular angular dependence of spin polarization. Following Cherepkov,[7] this angular dependence can also be presented in a vector form by writing it as products of unit vectors of $\mathbf{k}/|\mathbf{k}|$ and $\mathbf{s}/|\mathbf{s}|$ (to simplify the notation below, we use unnormalized vectors) and unit vector $\mathbf{q}$ related to the photon (Fig. 1). The resulting expression is

$$\begin{aligned} {}^{m^\gamma}I^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}''J''\eta''}(\mathbf{k},\mathbf{s})=\frac{1}{8\pi}\frac{N_E}{3}B^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}''J''\eta''}(\varepsilon)\Bigg[1&+\frac{2-3(m^\gamma)^2}{2}\beta^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}''J''\eta''}[\tfrac{3}{2}(\mathbf{k}\cdot\mathbf{q})-\tfrac{1}{2}]+m^\gamma\bar{P}^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}''J''\eta''}(\mathbf{s}\cdot\mathbf{q}) \\ &+m^\gamma\gamma^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}''J''\eta''}[\tfrac{3}{2}(\mathbf{k}\cdot\mathbf{s})(\mathbf{k}\cdot\mathbf{q})-\tfrac{1}{2}(\mathbf{s}\cdot\mathbf{q})]-[2-3(m^\gamma)^2]\xi^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}''J''\eta''}[\mathbf{s}\cdot(\mathbf{q}\times\mathbf{k})](\mathbf{q}\cdot\mathbf{k})\Bigg] , \end{aligned} \tag{21}$$

where the spin-polarization parameters are defined by the equations

$$\beta^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}''J''\eta''}(\varepsilon)=-\sqrt{2}C^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}''J''\eta''}(2,2,0,0,\varepsilon) , \tag{22}$$

$$\bar{P}^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}''J''\eta''}(\varepsilon)=\sqrt{3/2}C^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}''J''\eta''}(1,0,1,0,\varepsilon) , \tag{23}$$

$$\gamma^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}''J''\eta''}(\varepsilon)=-\sqrt{15/2}C^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}''J''\eta''}(1,2,1,0,\varepsilon) , \tag{24}$$

$$\xi^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}'' J'' \eta''}(\varepsilon) = \frac{3i}{2\sqrt{2}} [C^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}'' J'' \eta''}(2,2,1,-1,\varepsilon) - C^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}'' J'' \eta''}(2,2,1,1,\varepsilon)] \ . \tag{25}$$

The angular behavior of the cross section (21) is independent of the choice of a particular coordinate system. Moreover, it is formally the same for unpolarized atoms also.[7] The originality of the above expression stands in the explicit introduction of the initial- and final-state rotational levels, allowing the definition of a rotational state-to-state cross section.

Starting from simple scattering form (19), we can now single out the rotational factor (20d) and rewrite all the expressions for the polarization parameters (22)–(25). We explicitly give the expression for the $\bar{P}^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}'' J'' \eta''}(\varepsilon)$ parameter only:

$$\bar{P}^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}'' J'' \eta''}(\varepsilon) = \frac{3}{[J'']B^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}'' J'' \eta''}(\varepsilon)} \sum_{j_t} \sum_{\substack{\Omega'' \\ \tilde{\Omega}''}}{}' Q^{\bar{\Omega}_c J_c}_{\Omega'' \tilde{\Omega}'' J''}(j_t) c^{\bar{\Omega}_c J_c \eta_c}_{\Omega'' \tilde{\Omega}'' J'' \eta''}(1,0,1,j_t,\varepsilon) \ . \tag{26}$$

The general expression for the $c^{\bar{\Omega}_c J_c \eta_c}_{\Omega'' \tilde{\Omega}'' J'' \eta''}(1,0,1,j_t,\varepsilon)$ factor is given in Eq. (20c) and its particular form in Sec. IV [Eq. (31c)] below.

Up to now, we have discussed only the rotational state-to-state cross section and polarization parameters. Now we will average over the initial rotational states taking into account the Boltzmann distribution factor corresponding to a given temperature (see, e.g., Herzberg[33]):

$$N_{J''} = \frac{1}{Q_r}[J'']\exp[-B^{\text{in}}J''(J''+1)hc/(kT)] \ , \tag{27a}$$

where Q_r is given by

$$Q_r = \sum_{J''}^{\infty} [J'']\exp[-B^{\text{in}}J''(J''+1)hc/(kT)] \tag{27b}$$

and h, c, k, and T are the Planck constant, the speed of light, the Boltzmann constant, and the Kelvin temperature, respectively. B^{in} is the rotational constant of the initial state of the neutral molecule.

For each transition between initial and final rotational levels, we have to fulfill the following energy conservation expression:

$$E_{\text{ph}} = \Delta E^{\text{el}}_{C\Omega_c, n''\Omega''} + \Delta E^{\text{rot}}_{\Omega_c J_c, \Omega'' J''} + \varepsilon^{J_c}_{J''} \ , \tag{28}$$

where E_{ph} is the photon energy and $\Delta E^{\text{el}}_{C\Omega_c, n''\Omega''}$ and $\Delta E^{\text{rot}}_{\Omega_c J_c, \Omega'' J''}$ are electronic and rotational energy differences between the final and initial states. In Eq. (28) only transitions fulfilling the selection rules are considered. The kinetic energy of the photoelectron $\varepsilon^{J_c}_{J''}$ is implicitly a function of the other energy differences and is identical with the kinetic energy ε appearing for the first time in (10b) above.

Now, taking into account (28), we obtain the averaged cross section from a sum of expressions (19) or (20) each multiplied by the Boltzmann factor $N_{J''}$ (27):

$$\sigma^{\bar{\Omega}_c}_{\bar{\Omega}''}(E_{\text{ph}}) = \sum_{J_c} \sum_{\eta_c} \sum_{J''} \sum_{\eta''} \sigma^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}'' J'' \eta''}(\varepsilon^{J_c}_{J''}) N_{J''} \ , \tag{29a}$$

and similarly the averaged $\bar{P}$ polarization parameter:

$$\bar{P}^{\bar{\Omega}_c}_{\bar{\Omega}''}(E_{\text{ph}}) = \frac{\sum_{J_c} \sum_{\eta_c} \sum_{J''} \sum_{\eta''} \bar{P}^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}'' J'' \eta''}(\varepsilon^{J_c}_{J''}) \sigma^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}'' J'' \eta''}(\varepsilon^{J_c}_{J''}) N_{J''}}{\sum_{J_c} \sum_{\eta_c} \sum_{J''} \sum_{\eta''} \sigma^{\bar{\Omega}_c J_c \eta_c}_{\bar{\Omega}'' J'' \eta''}(\varepsilon^{J_c}_{J''}) N_{J''}} \ . \tag{29b}$$

All other polarization parameters can be written using formulas similar to (29b). We can also obtain a cross section intermediate between the state-to-state rotational cross section and the completely averaged one by omitting in (29) the summation over J_c, η_c, J'', and η''. As discussed above the summation over η'' and/or η_c signifies that we neglect Λ doubling in the initial and/or final states.

The averaged cross section and spin-polarization parameters (29) correspond to the photoabsorption spectrum. They will generate different spectra as a function of initial-state population, i.e., as a function of temperature. A striking example can be given in the case of photoionization of HI where warm (Eland and Berkowitz[35]) and cold spectra (Huth *et al.*[2] and Hart and Hepburn[3]) are very different.

IV. AN EXAMPLE: PHOTOIONIZATION OF HI MOLECULE

In order to illustrate the general formulas of the previous sections, we give here the explicit expressions for the total cross section and integrated spin-polarization parameter $\bar{P}$ in the particular case of photoionization of the HI molecule:

$$\begin{array}{lclcl} \text{HI}(^1\Sigma_0^+) + h\nu & \rightarrow & \text{HI}^+(^2\Pi_{3/2}) & + & e(l\lambda\sigma), \\ \Omega'' = 0 & & \Omega_c = \frac{3}{2} & & l = 0,1,2 \\ \eta'' = 1 & & \eta_c = \pm 1 & & \lambda = \sigma, \pi, \delta. \end{array} \tag{30}$$

Note that the HI molecule, on the one hand, is very close to an atom, allowing l, j, and j_t summations to be restricted to only a few terms, and on the other hand, is a molecule with a large rotational constant which is only ten times smaller than the rotational constant of the H_2 molecule. Therefore rotational features in the spectrum of the HI molecule are easily observable.

Below, we will use the scattering-form expressions (18), (20a), and (20e) for the cross section and (26) for the spin-polarization parameters as they are simpler to manipulate than the resonance-form ones.

In this example, we select one initial nondegenerate state n'' with $S''=0$ and $\Omega''=\tilde{\Omega}''=0$, and two final states with $C=(n_c\Lambda_c\Sigma_cS_c)=(n_c1\frac{1}{2};\frac{1}{2})$ and $\Omega_c=\frac{3}{2}$. The parity $\eta''=1$ of the initial and $\eta_c=\pm1$ of the final states correspond to the e and e,f states, respectively.[25] As a consequence, we simplify the notation (10c) for the transition moment $t_{n''\Omega''}^{\Omega_c,l\lambda}(\varepsilon)=t_{l\lambda}$ and notation (20e) for the coefficient $c_{\Omega''\tilde{\Omega}''J''\eta''}^{\bar{\Omega}_cJ_c\eta_c}\equiv c_{J''\eta''}^{J_c\eta_c}$. We also calculate explicitly all the 3-j symbols of Eqs. (20a), (20e), and (26). As we restrict $l\in[0,2]$, the angular momentum j and j_t are also restricted to $j\in[\frac{1}{2},\frac{5}{2}]$ and $j_t\in[\frac{3}{2},\frac{7}{2}]$.

The selection-rule factors give, for a particular selection of J'' and J_c, two distinct unequivalent contributions.

(i) One for $\eta''\eta_c(-1)^{-1/2+J_c+1+J''}=1$ and $\eta_{ll}=1$ which when introduced in (20e) gives

$$c_{J''\eta''}^{J_c\eta_c}(0,0,0,\tfrac{3}{2},\varepsilon_{J''}^{J_c})=|t_{s\sigma}|^2+\tfrac{7}{35}|t_{d\sigma}|^2+\tfrac{7}{21}|t_{d\pi}|^2+\tfrac{14}{21}|t_{d\delta}|^2+\frac{28}{35\sqrt{3}}\mathrm{Re}(t_{d\sigma}^*t_{d\pi})+\frac{56\sqrt{2}}{105}\mathrm{Re}(t_{d\pi}^*t_{d\delta})+\tfrac{14}{35}\sqrt{2/3}\,\mathrm{Re}(t_{d\sigma}^*t_{d\delta})\ , \tag{31a}$$

$$c_{J''\eta''}^{J_c\eta_c}(0,0,0,\tfrac{5}{2},\varepsilon_{J''}^{J_c})=\tfrac{18}{35}|t_{d\sigma}|^2+\tfrac{6}{21}|t_{d\pi}|^2+\tfrac{6}{21}|t_{d\delta}|^2+\frac{12}{35\sqrt{3}}\mathrm{Re}(t_{d\sigma}^*t_{d\pi})-\frac{36\sqrt{2}}{105}\mathrm{Re}(t_{d\pi}^*t_{d\delta})-\tfrac{24}{35}\sqrt{2/3}\,\mathrm{Re}(t_{d\sigma}^*t_{d\delta})\ , \tag{31b}$$

and

$$c_{J''\eta''}^{J_c\eta_c}(0,0,0,\tfrac{7}{2},\varepsilon_{J''}^{J_c})=\tfrac{10}{35}|t_{d\sigma}|^2+\tfrac{8}{21}|t_{d\pi}|^2+\tfrac{1}{21}|t_{d\delta}|^2-\frac{40}{35\sqrt{3}}\mathrm{Re}(t_{d\sigma}^*t_{d\pi})-\frac{20\sqrt{2}}{105}\mathrm{Re}(t_{d\pi}^*t_{d\delta})+\tfrac{10}{35}\sqrt{2/3}\,\mathrm{Re}(t_{d\sigma}^*t_{d\delta})\ . \tag{31c}$$

(ii) The other for $\eta''\eta_c(-1)^{-1/2+J_c+1+J''}=-1$, $\eta_{ll}=-1$, which when introduced in the same equation gives

$$c_{J''\eta''}^{J_c\eta_c}(0,0,0,\tfrac{3}{2},\varepsilon_{J''}^{J_c})=\tfrac{3}{5}|t_{p\sigma}|^2+\tfrac{3}{5}|t_{p\pi}|^2+\tfrac{4}{5}\mathrm{Re}(t_{p\sigma}^*t_{p\pi})\ , \tag{32a}$$

$$c_{J''\eta''}^{J_c\eta_c}(0,0,0,\tfrac{5}{2},\varepsilon_{J''}^{J_c})=\tfrac{2}{5}|t_{p\sigma}|^2+\tfrac{2}{5}|t_{p\pi}|^2-\tfrac{4}{5}\mathrm{Re}(t_{p\sigma}^*t_{p\pi})\ , \tag{32b}$$

and

$$c_{J''\eta''}^{J_c\eta_c}(0,0,0,\tfrac{7}{2},\varepsilon_{J''}^{J_c})=0\ . \tag{32c}$$

If now we restrict the initial rotational state population to only three rotational levels, i.e., $J''=0,1,2$, which corresponds approximately to a temperature of 20 K, then the allowed rotational levels of the ion for the $\Omega_c=\frac{3}{2}$ state are $J_c\in[\frac{3}{2},\frac{11}{2}]$. It is impossible to give here the expressions for all the corresponding transitions. Instead, we list the most intense transitions selected from a preliminary calculation[36] in the spin-orbit autoionization energy range using the same electronic model as the one published in Ref. 9, namely,

$$J''=0,\quad \eta''=1\quad\rightarrow\quad J_c=\tfrac{3}{2},\quad \eta_c=1, \tag{33a}$$

$$\begin{aligned} J''=1,\quad \eta''=1\quad\rightarrow\quad & J_c=\tfrac{3}{2},\quad \eta_c=-1,\\ & J_c=\tfrac{5}{2},\quad \eta_c=1, \end{aligned} \tag{33b}$$

$$\begin{aligned} J''=2,\quad \eta''=1\quad\rightarrow\quad & J_c=\tfrac{5}{2},\quad \eta_c=-1,\\ & J_c=\tfrac{3}{2},\quad \eta_c=1,\\ & J_c=\tfrac{7}{2},\quad \eta_c=1. \end{aligned} \tag{33c}$$

The above list establishes a propensity rule for these transitions. From this list, we explicitly present below the total cross section in the case of $J''=1$ which is the level with the highest population (47%) at the temperature of 20 K. The four resulting rotational factors, calculated using Eq. (20d) with $\Omega''=\tilde{\Omega}''=0$, have the following numerical values:

$$Q_0^{3/2}{}_1^{3/2}(3/2)=1.8,\quad Q_0^{3/2}{}_1^{3/2}(5/2)=0.8\ , \tag{34a}$$

$$\begin{aligned} Q_0^{3/2}{}_1^{5/2}(3/2)=1.2,\quad & Q_0^{3/2}{}_1^{5/2}(5/2)=0.7714\ ,\\ & Q_0^{3/2}{}_1^{5/2}(7/2)=1.0714\ . \end{aligned} \tag{34b}$$

The corresponding two cross sections are

$$\sigma_0^{3/2}{}_1^{3/2}{}_1^{-1}(\varepsilon_1^{3/2})=\frac{N_E}{9}[1.8c_1^{3/2}{}_1^{-1}(0,0,0,\tfrac{3}{2},\varepsilon_1^{3/2})+0.8c_1^{3/2}{}_1^{-1}(0,0,0,\tfrac{5}{2},\varepsilon_1^{3/2})]\ , \tag{35a}$$

$$\sigma_0^{3/2}{}_1^{5/2}{}_1^{1}(\varepsilon_1^{5/2})=\frac{N_E}{9}[1.2c_1^{5/2}{}_1^{1}(0,0,0,\tfrac{3}{2},\varepsilon_1^{5/2})+0.7714c_1^{5/2}{}_1^{1}(0,0,0,\tfrac{5}{2},\varepsilon_1^{5/2})+1.0714c_1^{5/2}{}_1^{1}(0,0,0,\tfrac{7}{2},\varepsilon_1^{5/2})]\ , \tag{35b}$$

where we have used Eqs. (31a) and (31b), respectively.

An expression for the spin-polarization parameter $\bar{P}$ analogous to the cross section (18), (20a), and (20e) was given in Eq. (26). The $c_{J''\eta''}^{J_c\eta_c}(1,0,1,j_t,\varepsilon_{J''}^{J_c})$ coefficient can be written in a simpler way than the general form (20c):

$$c_{J''\eta''}^{J_c\eta_c}(1,0,1,j_t,\varepsilon_{J''}^{J_c})=\sum_{l,j_1,j_2}(-1)^{l+j_t+1}[j_1,j_2]^{1/2}\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & 1\\ j_1 & j_2 & l\end{Bmatrix}\begin{Bmatrix}1 & 1 & 1\\ j_1 & j_2 & j_t\end{Bmatrix}\mathcal{S}_{S''J''\eta''}^{S_cJ_c\eta_c}(l,l)$$
$$\times\langle\overline{\Omega}_c,lj_1|T(j_t)|\Omega''\rangle\langle\Omega''|T(j_t)|\overline{\Omega}_clj_2\rangle\ . \tag{36}$$

Using this expression, we find again two distinct unequivalent contributions:

$$c_{J''\eta''}^{J_c\eta_c}(1,0,1,\tfrac{3}{2},\varepsilon_{J''}^{J_c})=-\tfrac{1}{6}|t_{s\sigma}|^2-\tfrac{7}{210}|t_{d\sigma}|^2-\tfrac{7}{315}|t_{d\pi}|^2+\tfrac{98}{630}|t_{d\delta}|^2-\frac{14\sqrt{3}}{315}\mathrm{Re}(t_{d\sigma}^{*}t_{d\pi})-\frac{14\sqrt{6}}{630}\mathrm{Re}(t_{d\sigma}^{*}t_{d\delta})$$
$$+\frac{28\sqrt{2}}{630}\mathrm{Re}(t_{d\pi}^{*}t_{d\delta})\ , \tag{37a}$$

$$c_{J''\eta''}^{J_c\eta_c}(1,0,1,\tfrac{5}{2},\varepsilon_{J''}^{J_c})=-\tfrac{18}{210}|t_{d\sigma}|^2+\tfrac{27}{315}|t_{d\pi}|^2+\tfrac{12}{630}|t_{d\delta}|^2-\frac{6\sqrt{3}}{315}\mathrm{Re}(t_{d\sigma}^{*}t_{d\pi})+\frac{24\sqrt{6}}{630}\mathrm{Re}(t_{d\sigma}^{*}t_{d\delta})-\frac{48\sqrt{2}}{630}\mathrm{Re}(t_{d\pi}^{*}t_{d\delta})\ , \tag{37b}$$

and

$$c_{J''\eta''}^{J_c\eta_c}(1,0,1,\tfrac{7}{2},\varepsilon_{J''}^{J_c})=-\tfrac{10}{210}|t_{d\sigma}|^2-\tfrac{20}{315}|t_{d\pi}|^2-\tfrac{5}{630}|t_{d\delta}|^2+\frac{20\sqrt{3}}{315}\mathrm{Re}(t_{d\sigma}^{*}t_{d\pi})-\frac{10\sqrt{6}}{630}\mathrm{Re}(t_{d\sigma}^{*}t_{d\delta})+\frac{20\sqrt{2}}{630}\mathrm{Re}(t_{d\pi}^{*}t_{d\delta})\ , \tag{37c}$$

for the case of $\eta''\eta_c(-1)^{-1/2+J_c+1+J''}=1$ and $\eta_{ll}=1$, and

$$c_{J''\eta''}^{J_c\eta_c}(1,0,1,\tfrac{3}{2},\varepsilon_{J''}^{J_c})=-\tfrac{3}{30}(t_{p\sigma})^2+\tfrac{1}{15}(t_{p\pi})^2-\tfrac{2}{15}\mathrm{Re}(t_{p\sigma}^{*}t_{p\pi})\ , \tag{38a}$$

$$c_{J''\eta''}^{J_c\eta_c}(1,0,1,\tfrac{5}{2},\varepsilon_{J''}^{J_c})=-\tfrac{2}{30}(t_{p\sigma})^2-\tfrac{1}{15}(t_{p\pi})^2+\tfrac{2}{15}\mathrm{Re}(t_{p\sigma}^{*}t_{p\pi})\ , \tag{38b}$$

$$c_{J''\eta''}^{J_c\eta_c}(1,0,1,\tfrac{7}{2},\varepsilon_{J''}^{J_c})=0\ , \tag{38c}$$

for the case of $\eta''\eta_c(-1)^{-1/2+J_c+1+J''}=-1$ and $\eta_{ll}=-1$.

Now, using Eqs. (37) and (38), we obtain the spin-polarization parameter $\bar{P}$ corresponding to the transition (33b):

$$\bar{P}_{0\ 1\ 1}^{3/2\ 3/2\ -1}(\varepsilon_1^{3/2})=\frac{1}{3B_{0\ 1\ 1}^{3/2\ 3/2\ -1}}[1.8c_{1\ 1}^{3/2\ -1}(1,0,1,\tfrac{3}{2},\varepsilon_1^{3/2})+0.8c_{1\ 1}^{3/2\ -1}(1,0,1,\tfrac{5}{2},\varepsilon_1^{3/2})]\ , \tag{39a}$$

$$\bar{P}_{0\ 1\ 1}^{3/2\ 5/2\ 1}(\varepsilon_1^{5/2})=\frac{1}{3B_{0\ 1\ 1}^{3/2\ 5/2\ 1}}[1.2c_{1\ 1}^{5/2\ 1}(1,0,1,\tfrac{3}{2},\varepsilon_1^{5/2})+0.7714c_{1\ 1}^{5/2\ 1}(1,0,1,\tfrac{5}{2},\varepsilon_1^{5/2})+1.0714c_{1\ 1}^{5/2\ 1}(1,0,1,\tfrac{7}{2},\varepsilon_1^{5/2})]\ . \tag{39b}$$

The formulas (35) and (39) give workable expressions for the example we have considered in this section. From these formulas and the one derived in Sec. III, we can draw the following conclusions.

(i) The particular rotational transition selects contributions given either by Eqs. (31) and (37) or by Eqs. (32) and (38). Therefore state-to-state rotational transition selects even or odd l of the spherical-harmonics expansion (2) related to the photoelectron momentum. This means that, using the rotational state-to-state spectroscopy, we can probe directly details of the photoelectron wave function. This result was already obtained theoretically[20,21,29] and confirmed experimentally (see Ref. 5 and references therein) in the case of resonant enhanced multiphoton ionization spectroscopy particularly for the NO molecule.[5,37] By using spin polarization of the photoelectron and differential cross section even more detailed probing of the photoelectron wave function is possible.

(ii) There are more terms in (31) and (37) than in (32), and (38). This is due only to the truncation in the expansion we have considered (two even l and one odd l) and has no particular physical meaning.

(iii) The cross terms appearing in the expressions (31), (32), (37), and (38) correspond to different projections of l on the internuclear axis, projections which are undefined in the space-fixed frame. As expected, molecular rotation mixes these different projections. But there are no cross terms in l, and consequently no long-range Coulomb phase differences. The integrated cross sections and spin polarization $\bar{P}$ are therefore probing only short-range phase differences. This property can be used for a more detailed analysis of phase differences contributing to the spectra by comparing integrated and differential cross sections and spin-polarization parameters.

(iv) If in a photoabsorption experiment the rotational structure is not resolved[35] then the corresponding cross section and polarization parameter formulas are, to a good approximation, obtained using (29) where we sum over final rotational levels J_c and parity η_c and average over initial rotation levels J'' and parity η'' but neglect the rotational energy differences $\Delta E_{\Omega_cJ_c,\Omega''J''}^{\mathrm{rot}}$ defined in (28). In order to demonstrate that we recover the purely electronic cross section (i.e., the sum of square moduli of electronic transition moments) we change the order of summations over J_c and j_t in the rotationally resolved cross section. Then, using orthogonality properties of 3-j symbols [see, e.g. Eq. (1.13) of Rotenberg *et al.*[28]], we obtain

$$\sum_{\eta_c}\sum_{J_c} Q^{\bar{\Omega}_c J_c}_{\Omega''\tilde{\Omega}''J''}(j_t)=[J''] .$$

Finally, by inspection, we can see that summation over j_t in (31) and (32) gives, for the cross section without rotation, only squares of moduli of transition moments, i.e., all the cross terms vanish. In the case of spin-polarization parameter $\bar{P}$, the same arguments hold, for (26) and the cross terms in (37) and (38) vanish also. The result is a sum of square moduli of transition moments with positive and negative signs, a standard situation without rotation. Using directly the formula without spin derived by Buckingham, Orr, and Sichel[11] and Sichel[12] we find a similar property for their rotationally unresolved cross section. These arguments are strictly valid if we neglect the energy difference between rotational levels of the initial and final states.

(v) If the rotational structure in a photoabsorption experiment is resolved[2,3] we have to take into account in (29) the energy difference $\Delta E^{\text{rot}}_{\Omega_c J_c,\Omega'' J''}$ and add it to the electronic transition energy $\Delta E^{\text{el}}_{C\Omega_c,n''\Omega''}$ defined in (28). Then the transition moments $t_{l\lambda}$, calculated at different kinetic energies $\varepsilon^{J_c}_{J''}$ [see (28)], contribute to the cross section at a given photon energy E_{ph}. Now, if the transition moments vary smoothly with the energy, the resulting photoabsorption cross section is approximately equal to the electronic cross section or the one obtained in the approximation of (iv). If there are narrow resonances in the photoabsorption spectrum, i.e., the transition moment varies sharply with the energy, then these two cross sections are very different. Namely, a single resonance corresponding to a purely electronic transition will split in several resonances in the present photoabsorption spectrum. Moreover, the cross terms in (31), (32), and (36)–(39) will not vanish as in the case of approximation (iv).

This short discussion completes the formulas presented in this section for the particular case of photoionization of the HI molecule from its ground state.

V. CONCLUSIONS

In this paper we have derived general expressions for the total and differential cross section and spin-polarization parameters for transitions from a given initial rotational level of the neutral molecule to a given final ionic rotational level. We started from the frame transformation between the laboratory frame corresponding to the experiment and the molecular frame where the actual numerical calculations are performed. The continuum electron wave function is expanded in spherical harmonics related to the position vector **r** and the momentum vector **k**. For the present analytic derivation of the differential cross section one needs only the explicit expansion of the wave function related to the momentum vector **k**.

Throughout this paper, we have used wave functions of definite parity. These functions are eigenfunctions of the total Hamiltonian and are essential when taking into account the rotation.

We used two angular momentum coupling schemes which correspond to different dummy summations, one over the transferred angular momentum j_t, the other one over the total angular momentum J of the final state (ion plus electron).

Our definition of j_t is slightly different from the one introduced by some authors.[14] Here j_t is the momentum transferred between the two fragments, electron and ion, including spin during the "half collision" process. The present definition of j_t was already discussed by us in Ref. 38 and also by Chandra.[39] It presents the advantage of being directly related to the expressions without spin.[11–13] The differential cross section in terms of j_t (the scattering form) is very simple since it contains an incoherent sum over j_t and a compact rotational factor, common for all the polarization parameters.

The differential cross section in terms of J (the resonance form), though having a more complicated expression, is appropriate for the interpretation of narrow resonances. In this case, a single term in the sum over J, having the same J as the discrete state embedded in the continuum, dominates the cross section.

An advantage of the present formulation, common to the two schemes, concerns the selection-rule factor. This factor, appearing in all the final formulas, permits us an easy evaluation of selection rules and of terms contributing to the transition moment and cross section. A particular experiment involving transition between two rotational levels can select only even or odd l in the cross section. Similar results were also obtained in the derivation of multiphoton ionization selection rules.[20,21,29]

The vector form of the differential cross section is presented in Eq. (21). This form associates the five polarization parameters to products of vectors defining the physical problem, thus making them independent of the coordinate system. It is common for unpolarized atoms,[7] for molecules in a gas phase both without rotation,[8,10] and, as it was done here, with rotation taken into account.

An expression for the differential photoionization cross section, which corresponds to the average over the initial Boltzmann distribution of the rotational levels and sum over the final rotational levels, have also been derived. The resulting spectrum will show splitting of the narrow electronic resonances into different rotational branches.

The formulas derived in this paper apply also to the $(n+1)$ multiphoton ionization if only the last ionization step is considered explicitly. The multiphoton experiments[5] have the advantage of populating only one rotational level of the intermediate state, thus considerably simplifying the spectrum and allowing the direct application of our very detailed formulas including spin polarization of the photoelectron. Alignment and orientation of the intermediate state, which often appears in multiphoton experiments,[5] can be easily taken into account in the present formulation.[37]

In the last section we derived explicit scattering-form formulas for the cross section and polarization parameter

$\bar{P}$ in the case of a restricted number of terms in these expressions. In particular, these formulas apply to the spin-orbit autoionization region of the photoionization of the HI molecule.

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