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Photoelectron spectroscopic studies of polyatomic molecules: Theory for spin polarization

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A general, nonrelativistic, multichannel theory for angle- and spin-resolved photoelectron spectroscopy of polyatomic molecules in the electric dipole approximation has been developed. Expressions for angular distribution of electrons ejected with defined spin polarization, both in molecule- and laboratory-fixed frames of reference from molecular targets with fixed as well as with random orientation in space, are derived. The transformation properties of the molecular point symmetry group are used to their full advantage to reduce these expressions to their simplest possible forms. The ionization amplitude is thus shown to decompose into a sum of transitions each involving the final-state wave function belonging to an irreducible representation of the point group of the target molecule. The formulas obtained herein can therefore be used to study spin-resolved photoionization in both linear and nonlinear molecules of any symmetry corresponding to one of the 32 point groups, either in their gaseous phase or oriented on liquid and solid surfaces. In order to study both the angular distribution as well as the degree of spin polarization of photoelectrons in terms of alternative contributions of the angular momentum transfer ($\mathbf{j}_t$) from photon to the ejected electron, a new set of ionization amplitudes is introduced whose contributions to the angular distribution add incoherently. This new approach not only simplifies the resulting expressions, but also eliminates the interference terms $j_t \neq j_t'$ which were present in an earlier expression for angular distribution of spin-polarized atomic photoelectrons. The theory developed in this paper has been used in the accompanying article to analyze photoionization in a nonlinear molecule whose point symmetry group is T_d.

I. INTRODUCTION

In order to obtain a complete understanding of the photoionization dynamics in atoms and molecules, an analysis of the angular distribution of electrons with defined spin polarization is needed. Such angle- and spin-resolved photoelectron spectroscopic (ASRPES) studies as a function of the wavelength of the incident radiation are essential to investigate the influence of the spin-orbit interaction (SOI) on dynamics of photoionization and also to determine both the magnitude and the phase of the transition moments. The availability of intense tunable radiation from synchrotron sources, combined with the advent of high-resolution, angle- and spin-resolving electron spectrometers, have made such studies experimentally possible.[1-7] The ASRPES measurements on atoms, along with related theoretical developments, have been in vogue for quite some time.[2-5] Those investigations have provided significant insight into the dynamical aspects of atomic photoionization.

The photoionization studies in diatomic as well as polyatomic (both linear and nonlinear) molecules, on the other hand, have primarily been confined so far to determining the behavior with photon wavelength of integrated and differential cross sections of electrons ejected without spin selection.[6,7] However, recent experiments by Heinzmann *et al.*[2,8,9] and by Schonhense *et al.*[10] have shown that, similar to the atomic case, spin-polarized photoelectrons can be produced also from randomly oriented linear as well as nonlinear molecules if the incident photon flux is circularly or linearly polarized, or even unpolarized. The spin polarization of electrons ejected by photoionization in CO_2, N_2O, CH_3Br, and in Br_2, I_2, CH_3Br, and CH_3I have, respectively, been measured by Heinzmann *et al.*[8,9] and by Schonhense *et al.*[10]

Simultaneous to these experimental investigations, Cherepkov[5,11] has developed expressions for angle- and spin-resolved photoionization in linear molecules with arbitrary orientation in space. This formulation has been applied by Lefebvre-Brion *et al.*[12] for the calculation of the two spin-polarization parameters for photoionization of HI in the spin-orbit autoionization region between the two $^2\Pi$ thresholds of the ionic ground state. Raseev *et al.*,[13] on the other hand, have extended Cherepkov's work[5,11] from the Hund's coupling scheme (a) to the scheme (c) for the description of the residual ionic state of a linear molecule and used[13] it to calculate the spin-polarization parameters in the case of π np outer-shell and d inner-shell photoionization of HBr and HI diatomics. Cherepkov[14] and Cherepkov and Kuznetsov[15,16] have further extended earlier work[5,11] from freely rotating targets to photoionization in molecules with fixed orientation in space.

While there have thus been several[11-16] ASRPES studies of linear molecules, the theories appropriate for similar investigations in nonlinear targets, on the other hand, are just beginning to emerge.[16] The basic difference between the linear and nonlinear systems comes from the fact that the molecular field in the latter case is no longer cylindrically symmetric. The loss of this symmetry results in two additional complications in nonlinear targets. (i) The projection m of the electronic orbital angular

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momentum l along the axis of the highest symmetry in a molecule (i.e., the molecular axis) ceases to be a good quantum number. Consequently, neither can the electronic energy levels nor the molecular orbitals be specified by the axial angular momentum m. (ii) The spherical harmonics are no longer the basis angular functions for the molecular orbitals.

This situation is further complicated if one needs to take into account the SOI in order to explain the spin polarization of photoelectrons, because the spin functions will now be molecule fixed and hence be affected by the symmetry of the target.[17]

Molecules of different symmetry are known to have different spectroscopic and other properties. The symmetry considerations therefore become fundamentally imperative whenever polyatomic molecules are the objects of a study. These are of much greater importance for nonlinear systems than for linear ones, since for the former many more different types of symmetry (i.e., point groups) are possible than for the latter, which display only the $D_{\infty h}$ (homonuclear) and the $C_{\infty v}$ (heteronuclear) varieties.

The symmetry properties of a molecule can be properly accounted for by taking recourse to the powerful methods of the theory of point groups. For example, a molecule will have as many kinds of bound or continuum orbitals as there are irreducible representations (IR's) in its point group. Both the energy levels and orbitals in a nonlinear molecule are specified by the corresponding IR's.

Furthermore, there are well-developed purely angular[18] and coupled angular-spin[19] functions which transform according to the various IR's of the point group to which they belong. These symmetry-adapted functions form a complete set whose members diagonalize the molecular Hamiltonian without[18] or with[19] SOI. These functions provide a most natural and convenient basis set both for the bound and the continuum molecular orbitals.

It is probably for these and other similar reasons that both quantum chemists and solid-state physicists have long been using group-theoretical methods in their respective fields of study. These methods were applied, probably for the first time, to the continuum process of electron scattering from polyatomic molecules by Burke *et al.*[20] This theory has since then been used quite successfully to study both electron and positron scattering from a number of nonlinear molecular targets.[21] Group-theoretical techniques have also been recently adapted to angle-resolved photoelectron spectroscopic (ARPES) studies of polyatomic molecules.[22] Application of this theory to angular distribution of spin-unresolved electrons ejected by photoionization in the electric dipole ($E1$) approximation from both freely rotating[23-25] and oriented[26-29] nonlinear molecules has been very encouraging.

In this paper we further develop these group-theoretical approaches by formulating a multichannel, nonrelativistic theory for ASRPES of polyatomic molecules with fixed as well as random orientation in space. (A short early account of this work has been presented elsewhere.[30]) The interaction of the incident radiation with the target is treated in the $E1$ approximation. The various formulas derived herein are in their most general forms and can be used for photoionization in any molecule, linear or nonlinear, belonging to one of the 32 point groups.

Furthermore, it is well known that studies of photoelectron angular distributions constitute a sensitive probe of the anisotropic interaction between the residual ion and the ejected electron. A theory for photoionization should therefore be capable of properly analyzing this electron-ion final-state interaction. The expressions for angular distribution of photoelectrons, on the other hand, have a very complicated structure because of the presence of a large number of coherent sums. In order to simplify these formulas so that the electron-ion-interaction mechanism becomes as transparent as possible, Fano and Dill,[31] Dill and Fano,[32] and Dill[33] introduced a new set of ionization amplitudes specified by

$$\mathbf{t} = \mathbf{l}_r - \mathbf{l} = \mathbf{J}_f + \mathbf{s} - \mathbf{J}_b \tag{1}$$

in the context of spin-unresolved photoionization. Here, $\mathbf{l}_r$ ($|\mathbf{l}_r| = 1$ for an $E1$ process) is the angular momentum of the incident radiation; $\mathbf{l}$ is the orbital and $\mathbf{s}$ the spin-angular momenta of the photoelectron; $\mathbf{J}_b$ and $\mathbf{J}_f$ are, respectively, the angular momenta of the initial bound state and of the final ionic state after photoionization of the atomic or molecular target. The vector $\mathbf{t}$ is the angular momentum transferred from the photon to the ejected electron. The resulting photoelectron angular distribution in terms of the new set of transition amplitudes specified by t was much simpler, because a large number of coherent sums present in the original expression were replaced by a single incoherent sum over t.

Hitherto, a theory for angular distribution of spin-resolved photoelectrons in terms of angular momentum transfer has only been formulated by Klar[34] in the context of atomic photoionization. Unfortunately, Klar's extension of the Fano-Dill work[31-33] contains,[34] in place of a single sum over t, two coherent sums over t and t'. The presence of interference terms with $t \neq t'$ increases the complexity of the angular distribution formulas, hence making them less useful as well as transparent for analyzing the electron-ion interaction.

It has already been pointed out[32,33] that Eq. (1) defines that angular momentum which is exchanged between the *unobserved* initial and final angular momenta involved in a photoionization process, i.e., between $\mathbf{J}_b$ and $\mathbf{J}_f + \mathbf{s}$. The definition (1) of $\mathbf{t}$ is therefore no longer valid for those photoionization experiments in which the spin of the ejected electron is also detected. In this paper we therefore introduce a new angular momentum transfer $\mathbf{j}_t$ to study the spin polarization of photoelectrons. Since the ejected electron is observed with its spin, we therefore define

$$\mathbf{j}_t = \mathbf{l}_r - \mathbf{j} = \mathbf{J}_f - \mathbf{J}_b, \quad \mathbf{j} \equiv \mathbf{l} + \mathbf{s} . \tag{2}$$

This analysis results in a much simpler expression where a large number (more than ten) coherent sums present in the original formulas for angular distribution of spin-polarized molecular photoelectrons are replaced by two coherent and two incoherent sums. More importantly, because there is now a single sum over j_t, the final expression does not contain the interference term $j_t \neq j_t'$.

In one of his recent papers with Kuznetsov, Cherepkov[16] has also discussed the angular distribution of photoelectrons with defined spin polarization ejected from molecules of relatively low symmetry. However, their treatment is very different from the one given here in several respects: First, Cherepkov and Kuznetsov[16] have used the independent-particle model of Cooper and Zare,[35] extending it from unpolarized to polarized photoelectrons. Their[16] approach therefore does not include the anisotropic interactions between the residual ion and the photoelectron, which have been found to be very important[36] but are completely ignored in the Cooper-Zare model.[35] Second, similar to their other papers,[11,14,15] the theory developed by Cherepkov and Kuznetsov[16] is most suitable for linear molecules which can belong to either $C_{\infty v}$ or $D_{\infty h}$ point groups. It is because they[16] expand molecular orbitals in terms of spherical harmonics which form a natural angular basis for an electron moving in a cylindrically symmetric field. It will be a very difficult task to introduce in their[16] formulation those symmetry elements which do not occur in $C_{\infty v}$ or $D_{\infty h}$ targets, but are known to be present in general in a very large number of molecules, in order to adapt the expressions derived by Cherepkov and Kuznetsov[16] to angle- and spin-resolved photoionization in molecular systems belonging to other than these two linear point groups.

It has already been pointed out in this paper that symmetry considerations are of crucial importance for proper understanding of any physical process taking place in a nonlinear system. In the absence of such adaptations, the treatment developed by Cherepkov and Kuznetsov[16] becomes very difficult to use. More importantly, one will not be able to identify in their[16] formulation the symmetries and the kind of molecular orbitals participating in a reaction to be studied. Furthermore, because Cherepkov and Kuznetsov[16] have not developed their theory in terms of angular momentum transfer, the expressions derived by them are in very complicated forms as they contain a large number of coherent sums. On the other hand, the present theory, which is a multichannel treatment of ASRPES of nonlinear molecules in its most general form, is free from all such weaknesses.

We first obtain, in the next section, an expression for the final state of the postphotoionization system $e+M^+$, where M^+ is the residual ion of the target molecule M. Section III presents the angular distribution of spin-polarized photoelectrons ejected from nonlinear systems in both molecule- and laboratory-fixed frames of reference. In order to obtain photoelectron angular distribution for ionization in randomly oriented (i.e., freely rotating) targets, the expressions derived in Sec. III are averaged over all possible orientations of a molecule in space in Sec. IV. Section V, on the other hand, presents the angular momentum transfer treatment of the ASRPES in molecules using the coupling scheme introduced in Eq. (2). The analyses of the angular distribution and of the degree of spin polarization of the photoelectrons is carried out in Secs. VI and VII, respectively. The last section, Sec. VIII, contains the conclusion of this study. The theory developed in this paper has been applied in the following article[37] to study in detail photoionization in a bound orbital belonging to the A_1 IR of a randomly oriented T_d molecule.

II. FINAL-STATE WAVE FUNCTION

In order to develop a theory for ASRPES of a polyatomic molecule, one requires a wave function for the $e+M^+$ system. This function, while representing the molecular residue M^+, should describe the departing electron with its directions of propagation and of spin polarization. For a general multichannel formulation, we define a complete set of basis channel functions

$$\Psi_{hl\nu}^{p\tau-} = \mathcal{A}(\Psi_f F_{hl\nu}^{p\tau-}) \tag{3}$$

which are solutions of the following Schrödinger equation:

$$H|\Psi_{hl\nu}^{p\tau-}\rangle = (E_f+\varepsilon_f)|\Psi_{hl\nu}^{p\tau-}\rangle \ . \tag{4}$$

Here $\mathcal{A}$ is the antisymmetrization operator, H is the Hamiltonian of the $e+M^+$ system containing the electrostatic interactions as well as the SOI's, Ψ_f is the electronic state of the residual ion M^+ with energy E_f, and

$$F_{hl\nu}^{p\tau-} = r^{-1} \sum_{h',l',\nu'} U_{hl\nu,h'l'\nu'}^{p-}(r) X_{h'l'}^{p\tau}(\hat{\mathbf{r}}) \Phi(\nu') \tag{5}$$

is the spin orbital of the ejected electron moving in the molecular continuum with energy ε_f. The superscript $-$ on a function indicates that it asymptotically satisfies the incoming-wave boundary conditions appropriate for photoionization.[38] $\Phi(\nu)$ in (5) is the spin function, i.e., the spinor

$$\Phi(\tfrac{1}{2}) = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \equiv \alpha, \quad \Phi(-\tfrac{1}{2}) = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \equiv \beta$$

of the photoelectron with spin component $\nu\hbar$ along the molecular axis. This axis is taken to be the polar (i.e., $0Z$) axis of the molecule- (body-) fixed frame of reference. The origin of the corresponding coordinate system is the center of mass of the molecule.

The angular parts $X_{hl}^{p\tau}(\hat{\mathbf{r}})$, called generalized harmonics (GH, or the basis angular functions),[18] in the spin orbital (5) transform according to the pth IR of the point group of the target M. While the dimensionality (i.e., the degeneracy) of this IR is represented by τ, its different bases belonging to the same value of l are distinguished by h. These GH can be written[18,20] in terms of linear combinations of spherical harmonics

$$X_{hl}^{p\tau}(\hat{\mathbf{r}}) = \sum_{m=-l}^{l} b_{hlm}^{p\tau} Y_l^m(\hat{\mathbf{r}}) \ , \tag{6}$$

where the b's are the appropriate expansion coefficients.[20] Finally, the radial functions in (5) satisfy the complex, asymptotic incoming-wave[38] boundary conditions

$$\lim_{r\to 0} U^{p-}_{hl\nu,h'l'\nu'}(r)=r^{l+1}\delta_{hh'}\delta_{ll'}\delta_{\nu\nu'} ,$$

$$\lim_{r\to\infty} U^{p-}_{hl\nu,h'l'\nu'}(r)$$

$$=i\left[\frac{m_e}{2\pi\hbar^2 k}\right]^{1/2}[e^{-i\vartheta_{l'}}(S^p)^{\dagger}_{hl\nu,h',l',\nu'}-e^{i\vartheta_l}\delta_{hh'}\delta_{ll'}\delta_{\nu\nu'}]$$

$$\text{for } k^2\left[=\frac{2m_e}{\hbar^2}\varepsilon_f\right]>0 , \quad (7)$$

$$\lim_{r\to\infty} U^{p-}_{hl\nu,h'l'\nu'}(r)=e^{-[|k|r+\eta\ln(2|k|r)]}\delta_{hh'}\delta_{ll'}\delta_{\nu\nu'}$$

$$\text{for } k^2<0 .$$

Here

$$\vartheta_l=kr-\tfrac{1}{2}l\pi-\eta\ln 2kr+\sigma_l ,$$

$$k\eta=-m_e\left[\sum_i Z_i-(n_e-1)\right]e^2/\hbar^2 , \quad (8)$$

with

$$\sigma_l=\arg[\Gamma(l+1+i\eta)] ,$$

the Coulomb phase and m_e the reduced mass of the photoelectron. Z_i in (8) is the charge of the ith nucleus present in the target molecule which contains n_e total number of electrons before ionization.

The required final-state function can now be expanded in terms of the channel state (3) using the procedures described earlier[22,39]

$$\Psi^-_{\mathbf{k}\nu}=\left[\frac{\hbar^2}{m_e}\right]^{1/2}\sum_{p,\tau,h,l} i^l e^{-i\sigma_l}[X^{p\tau}_{hl}(\hat{\mathbf{k}})]^*\Psi^{p\tau-}_{hl\nu} . \quad (9)$$

Here $\mathbf{k}(k,\theta,\phi)$ is the propagation vector of the photoelectron in the molecule frame of reference. The significant point about (9) is that both the functions $X^{p\tau}_{hl}(\hat{\mathbf{k}})$ and the expansion coefficients $\Psi^{p\tau-}_{hl\nu}$ transform according to the various IR's of the point group of the $e+M^+$ system.[40] The important implications of this property will become apparent when we derive expressions for the ionization amplitude in Sec. III. This final state has the following normalization:

$$\langle\Psi^-_{\mathbf{k}\nu}|\Psi^-_{\mathbf{k}'\nu'}\rangle=\delta(\varepsilon_f-\varepsilon_{f'})\delta_{ff'}\delta_{\nu\nu'}$$

which corresponds to the unit density of states in the continuum and the orthonormality of the discrete part of the $e+M^+$ system.

Let us assume for generality that the spin of the photoelectron is quantized along the unit vector $\hat{\mathbf{u}}(\theta_u,\phi_u)$ referred to the molecule-fixed frame with $\nu_0\hbar$ the projection of the spin angular momentum along this direction. A final state which describes the ejected electron in the $e+M^+$ system with spin quantization along $\hat{\mathbf{u}}$, rather than along $0Z$, is then given by

$$\Psi^-_{\mathbf{k}\nu_0}=\sum_{\nu}[\mathcal{D}^{1/2}_{\nu_0\nu}(\omega_u)]^*\Psi^-_{\mathbf{k}\nu} . \quad (10)$$

Here $\omega_u(\phi_u,\theta_u,0)$ are the Euler angles which rotate $\hat{\mathbf{u}}$ in coincidence with the $0Z$ axis of the molecule frame and the $\mathcal{D}$'s are the rotation matrices.[41] (Note that in both of the states $\Psi^-_{\mathbf{k}\nu}$ and $\Psi^-_{\mathbf{k}\nu_0}$ the photoelectron propagation direction $\mathbf{k}$ is the same.)

If one is interested in studying molecular photoionization in a laboratory frame, a final state for the $e+M^+$ system with both the propagation direction and the spin-quantization axis of the ejected electron referred to the photon frame of reference is needed. We introduce for this purpose a so-called photon (i.e., laboratory-) fixed frame of reference. The origin of this coordinate system is the same as that of the body frame, i.e., the center of mass of the target molecule; the polar $(0Z')$ axis of this new frame, on the other hand, is along the direction of electric vector (incidence) for linearly polarized (unpolarized, circularly polarized) light. Further, if (β,α) are the spherical polar angles of the $0Z$ axis with respect to the photon frame, rotations by the Euler angles $-\alpha,-\beta,-\gamma$ (collectively denoted by $\omega=\alpha\beta\gamma$) will bring the coordinate axes of the molecule frame in coincidence with those of the latter.[41] The space variables referred to the photon- (molecule-) fixed coordinate system, in the following, will be primed (unprimed).

If the spin of the photoelectron is quantized along the $0Z'$ axis with component $\mu\hbar$, the final state referred to in the photon frame is then given by

$$\Psi^-_{\mathbf{k}'\mu}=\left[\frac{\hbar^2}{m_e}\right]^{1/2}\sum_{\substack{p,\tau,h,l,\\ m,n,\nu}} i^l e^{-i\sigma_l}(b^{p\tau}_{hlm})^* \times\mathcal{D}^l_{mn}(\omega)[Y^n_l(\hat{\mathbf{k}}')]^* \times\mathcal{D}^{1/2}_{\nu\mu}(\omega)\Psi^{p\tau-}_{hl\nu} . \quad (11)$$

On the other hand, if the spin angular momentum of the ejected electron has a component $\mu_0\hbar$ along $\hat{\mathbf{u}}'(\theta_{u'},\phi_{u'})$ in the photon frame, we then obviously have

$$\Psi^-_{\mathbf{k}'\mu_0}=\sum_{\mu}[\mathcal{D}^{1/2}_{\mu_0\mu}(\omega_{u'})]^*\Psi^-_{\mathbf{k}'\mu}$$

$$=\left[\frac{\hbar^2}{m_e}\right]^{1/2}\sum_{\substack{p,\tau,h,l\\ m,n,\nu,\mu}} i^l e^{-i\sigma_l}(b^{p\tau}_{hlm})^*\mathcal{D}^l_{mn}(\omega)[Y^n_l(\hat{\mathbf{k}}')]^* \times[\mathcal{D}^{1/2}_{\mu_0\mu}(\omega_{u'})]^*\mathcal{D}^{1/2}_{\nu\mu}(\omega)\Psi^{p\tau-}_{hl\nu} , \quad (12)$$

where $\omega_{u'}(\phi_{u'},\theta_{u'},0)$ are the Euler angles which rotate the $\hat{\mathbf{u}}'$ direction in the $0Z'$ axis.

III. IONIZATION IN MOLECULES WITH FIXED ORIENTATION IN SPACE

A. Angular distribution in molecule frame of reference

The angular distribution of electrons ejected with spin component $\nu_0\hbar$ along $\hat{\mathbf{u}}$ into the solid angle $d\hat{\mathbf{k}}$ about the direction of propagation $\hat{\mathbf{k}}$ by photoionization in a polyatomic molecule whose orientation[42] in space is defined by the Euler angles ω can be written as[43]

$$\frac{d^2\sigma(m_r,\hat{\mathbf{u}},\nu_0)}{d\omega\, d\hat{\mathbf{k}}}=\frac{K}{W_b}\sum_{\mathrm{DS}}\left|\left[\frac{m_e}{\hbar^2}\right]^{1/2}\langle\Psi^-_{\mathbf{k}\nu_0}|F|\Psi_b,1m_r\rangle\right|^2 . \tag{13}$$

Here $K=3\pi(e^2/\alpha_0E_r)^2$, with α_0 the dimensionless fine-structure constant and E_r the energy of the incident radiation whose state of [linear or left (right) circular] polarization is specified by m_r [$=0$ or $+1$ (-1), respectively]. $|\Psi_b\rangle$ is the initial bound state of the molecule before ionization with the energy E_b related by $\varepsilon_f=(E_b+E_r)-E_f$, and with the statistical weight (degeneracy) W_b. The expression (13) includes sum over all degenerate states (DS) of both M and M^+. The relationship between the matrix elements of the photoionization operator F and those of the $E1$ operator of an n_e electron system are the same as described by us earlier[39,44] for photoionization in diatomic molecules.

On substituting the final-state function (10), using the expansions (6) and (9), the angular distribution (13) becomes

$$\frac{d^2\sigma(m_r,\hat{\mathbf{u}},\nu_0)}{d\omega\, d\hat{\mathbf{k}}}=\frac{K}{W_b}\sum_{\mathrm{DS}}\left|\sum_{p,\tau,h,l,m,\nu}(-i)^l e^{i\sigma_l} b^{p\tau}_{hlm}\,Y_l^m(\hat{\mathbf{k}})\mathcal{D}^{1/2}_{\nu_0\nu}(\omega_u)\langle\Psi^{p\tau-}_{hl\nu}|F|\Psi_b,1m_r\rangle\right|^2 . \tag{14}$$

Thus the ionization amplitude $\langle\Psi^-_{\mathbf{k}\nu_0}|F|\Psi_b,1m_r\rangle$ in (13) is decomposed in the distribution (14) into a sum of transitions each involving the continuum wave function for an IR belonging to the symmetry group of the $e+M^+$ system.[40] It has already been pointed out in Sec. I in this paper that orbitals in nonlinear targets are specified by the IR of the molecular point group. Thus the decomposition carried out in (14) makes possible not only the identification of the molecular orbitals which participate in photoionization, but also the calculation of their individual contribution to the actual physical process.[22–29] This result is a consequence of the relation (9) whereby both the channel functions $\Psi^{p\tau-}_{hl\nu}$ and the coefficients $X^{p\tau}_{hl}(\hat{\mathbf{k}})$ present in the expansion of the final state function $\Psi^-_{\mathbf{k}\nu}$ transform according to the various IR's of the point group of the $e+M^+$ system.

After substituting the expansion

$$|1m_r\rangle=\sum_{\lambda_r}\mathcal{D}^1_{\lambda_r m_r}(\omega)|1\lambda_r\rangle \tag{15}$$

for the photon state in the molecule frame and using the coupling rules[41] for the products of two $\mathcal{D}$ functions and of two spherical harmonics, the distribution (14) can be written in the following form:

$$\frac{d^2\sigma(m_r,\hat{\mathbf{u}},\nu_0)}{d\omega\, d\hat{\mathbf{k}}}=(-1)^{m_r+\nu_0}\frac{K}{W_b}\sum_{\mathrm{DS}}\sum_{L=0}^{2l_>}\sum_{M=-L}^{L}A_{LM}(\omega,\omega_u,m_r,\nu_0;k)Y_L^M(\hat{\mathbf{k}}) , \tag{16a}$$

with

$$\begin{aligned}
&A_{LM}(\omega,\omega_u,m_r,\nu_0;k)\\
&\quad=\sum_{\substack{p,\tau,h,l,m,\nu,\lambda_r,\\ p',\tau',h',l',m',\nu',\lambda'_r}}(-i)^{l-l'}e^{i(\sigma_l-\sigma_{l'})}(-1)^{m+\lambda_r-\nu}\left[\frac{(2l+1)(2l'+1)(2L+1)}{4\pi}\right]^{1/2}\\
&\qquad\times\begin{bmatrix} l & l' & L\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix} l & l' & L\\ -m & m' & M\end{bmatrix} b^{p\tau}_{hlm}(b^{p'\tau'}_{h'l'm'})^* d^{p\tau}_{hl\nu,b}(\lambda_r)[d^{p'\tau'}_{h'l'\nu',b}(\lambda'_r)]^*\\
&\qquad\times\sum_{S=0}^{1}\sum_{M_S=-S}^{S}(2S+1)\begin{bmatrix} \frac{1}{2} & \frac{1}{2} & S\\ -\nu_0 & \nu_0 & 0\end{bmatrix}\begin{bmatrix} \frac{1}{2} & \frac{1}{2} & S\\ -\nu & \nu' & M_s\end{bmatrix}\mathcal{D}^S_{0M_s}(\omega_u)\\
&\qquad\qquad\times\sum_{L_r=0}^{2}\sum_{M_r=-L_r}^{L_r}(2L_r+1)\begin{bmatrix} 1 & 1 & L_r\\ -m_r & m_r & 0\end{bmatrix}\begin{bmatrix} 1 & 1 & L_r\\ -\lambda_r & \lambda'_r & M_r\end{bmatrix}\mathcal{D}^{L_r}_{M_r0}(\omega)
\end{aligned} \tag{16b}$$

and $l_> = \max(l,l')$. Here

$$d^{p\tau}_{hl\nu,b}(\lambda_r) \equiv \langle \Psi^{p\tau -}_{hl\nu} | F | \Psi_b, 1\lambda_r \rangle = A^{(a)} \left\langle \Psi^{p\tau -}_{hl\nu} \left| \sum_{s=1}^{n_e} \hat{\xi}_{\lambda_r} \cdot \mathbf{Q}^{(a)}_s \right| \Psi_b \right\rangle \tag{17}$$

is the ionization amplitude with $\hat{\xi}_{\lambda_r}$ the spherical unit vector[41] in the direction of polarization of the photon beam in the molecule frame. The appropriate forms of the $E1$ operator $\mathbf{Q}^{(a)}_s$ and of the corresponding coefficients $A^{(a)}$ in both length $(a=1)$ and velocity $(a=2)$ approximations have been defined by us elsewhere.[39,44]

Equation (16) is the most general result for angular distribution of spin-resolved electrons ejected by photoionization in the $E1$ approximation in a polyatomic molecule held with a fixed orientation in space. This expression, which is probably in its simplest possible form, is equally applicable to photoionization in all molecular systems belonging to one of the 32 point groups. Because the orbital angular momentum is not a good quantum number in molecules, therefore, in principle, there should be an infinite number of partial waves (l,l') present in (16) to represent the departing electron. Hence this angular distribution contains six infinite sums over l,l',L,m $(=-l$ to $l)$, m' $(=-l'$ to $l')$, and M $(=-L$ to $L)$.

In order to obtain from (16) the angular distribution of photoelectrons without spin selection, one merely needs to sum it over $\nu_0 = \pm\frac{1}{2}$, i.e.,

$$\frac{d^2\sigma(m_r)}{d\omega\, d\hat{\mathbf{k}}} = \sum_{\nu_0} \frac{d^2\sigma(m_r,\hat{\mathbf{u}},\nu_0)}{d\omega\, d\hat{\mathbf{k}}} .$$

Because of the property[41]

$$\sum_{\nu_0} (-1)^{\nu_0} \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ -\nu_0 & \nu_0 & 0 \end{bmatrix} = (-1)^{-1/2}\sqrt{2}\,\delta_{0S} , \tag{18}$$

we therefore obtain

$$\frac{d^2\sigma(m_r)}{d\omega\, d\hat{\mathbf{k}}} = (-1)^{m_r} \frac{K}{W_b} \times \sum_{\mathrm{DS}} \sum_{L,M} \sum_{\substack{p,\tau,h,l,m,\lambda_r, \\ p',\tau',h',l',m',\lambda'_r}} (-i)^{l-l'} e^{i(\sigma_l - \sigma_{l'})} (-1)^{m+\lambda_r}$$
$$\times \left[\frac{(2l+1)(2l'+1)(2L+1)}{4\pi} \right]^{1/2} \begin{bmatrix} l & l' & L \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l & l' & L \\ -m & m' & M \end{bmatrix} b^{p\tau}_{hlm} (b^{p'\tau'}_{h'l'm'})^* Y^M_L(\hat{\mathbf{k}})$$
$$\times \sum_{L_r} (2L_r+1) \begin{bmatrix} 1 & 1 & L_r \\ -m_r & m_r & 0 \end{bmatrix} \begin{bmatrix} 1 & 1 & L_r \\ -\lambda_r & \lambda'_r & \lambda_r - \lambda'_r \end{bmatrix}$$
$$\times \mathcal{D}^{L_r}_{\lambda_r - \lambda'_r, 0}(\omega) \sum_{\nu} d^{p\tau}_{hl\nu,b}(\lambda_r) [d^{p'\tau'}_{h'l'\nu,b}(\lambda'_r)]^* . \tag{19}$$

This result is equivalent to Eq. (11) already derived by us for spin-unresolved photoionization in polyatomic molecules in Ref. 22.

The total spin-polarized photocurrent

$$\frac{d\sigma(m_r,\hat{\mathbf{u}},\nu_0)}{d\omega} = \int \frac{d^2\sigma(m_r,\hat{\mathbf{u}},\nu_0)}{d\omega\, d\hat{\mathbf{k}}} d\hat{\mathbf{k}} , \tag{20}$$

$$= (-1)^{m_r+\nu_0} \frac{K}{W_b} \sum_{\mathrm{DS}} \sum_{\substack{p,\tau,h,l, \\ \nu,\nu',\lambda_r,\lambda'_r}} (-1)^{\lambda_r - \nu} d^{p\tau}_{hl\nu,b}(\lambda_r) [d^{p\tau}_{hl\nu',b}(\lambda'_r)]^*$$
$$\times \sum_{\substack{S,M_S, \\ L_r,M_r}} (2S+1)(2L_r+1) \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ -\nu_0 & \nu_0 & 0 \end{bmatrix} \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ -\nu & \nu' & M_S \end{bmatrix}$$
$$\times \begin{bmatrix} 1 & 1 & L_r \\ -m_r & m_r & 0 \end{bmatrix} \begin{bmatrix} 1 & 1 & L_r \\ -\lambda_r & \lambda'_r & M_r \end{bmatrix} \mathcal{D}^S_{0M_S}(\omega_u) \mathcal{D}^{L_r}_{M_r 0}(\omega) , \tag{21}$$

produced by ionization in an oriented molecular target, involves only a single infinite sum over l.

B. Angular distribution in laboratory frame of reference

The angular distribution of electrons ejected in photon frame of reference, into the solid angle $d\hat{\mathbf{k}}'$ about the direction of propagation $\hat{\mathbf{k}}'$ and with the spin component μ_0 along the direction $\hat{\mathbf{u}}'$ from a molecule with fixed orientation ω in space can be obtained in two ways. One can either find it directly from the last subsection by making the following two substitutions:

$$Y_L^M(\hat{\mathbf{k}})=\sum_N [\mathcal{D}_{MN}^L(\omega)]^* Y_L^N(\hat{\mathbf{k}}')$$

and

$$\mathcal{D}_{0M_s}^S(\omega_u)=\sum_{N_S} [\mathcal{D}_{M_SN_S}^S(\omega)]^* \mathcal{D}_{0N_S}^S(\omega_{u'})$$

in (16). The other procedure is to follow the *ab initio* method used in Sec. III A to obtain angular distribution of polarized photoelectrons in molecule frame of reference. In this paper we shall, however, adopt the second procedure as it will also be useful to us in Sec. V as well.

The desired distribution is given by

$$\frac{d^2\sigma(m_r,\hat{\mathbf{u}}',\mu_0)}{d\omega\, d\hat{\mathbf{k}}'}=\frac{K}{W_b}\sum_{\mathrm{DS}}\left|\left[\frac{m_e}{\hbar^2}\right]^{1/2}\langle \Psi_{\mathbf{k}'\mu_0}^- | F | \Psi_b, 1m_r\rangle\right|^2 . \tag{22}$$

On substituting the final state (12) and the expansion (15), we obtain

$$\begin{aligned}\frac{d^2\sigma(m_r,\hat{\mathbf{u}}',\mu_0)}{d\omega\, d\hat{\mathbf{k}}'}=\frac{K}{W_b}\sum_{\mathrm{DS}}\sum_{\substack{p,\tau,h,l,m,n,\nu,\mu,\lambda_r,\\ p',\tau',h',l',m',n',\nu',\mu',\lambda_r'}} & (-i)^{l-l'}e^{i(\sigma_l-\sigma_{l'})}b_{hlm}^{p\tau}(b_{h'l'm'}^{p'\tau'})^*\mathcal{D}_{\mu_0\mu}^{1/2}(\omega_{u'})\\ & \times[\mathcal{D}_{\mu_0\mu'}^{1/2}(\omega_{u'})]^*[\mathcal{D}_{\nu\mu}^{1/2}(\omega)]^*\mathcal{D}_{\nu'\mu'}^{1/2}(\omega)[\mathcal{D}_{mn}^{l}(\omega)]^*\mathcal{D}_{m'n'}^{l'}(\omega)\\ & \times\mathcal{D}_{\lambda_r m_r}^{1}(\omega)[\mathcal{D}_{\lambda_r' m_r}^{1}(\omega)]^*d_{hl\nu,b}^{p\tau}(\lambda_r)[d_{h'l'\nu',b}^{p'\tau'}(\lambda_r')]^*Y_l^n(\hat{\mathbf{k}}')[Y_{l'}^{n'}(\hat{\mathbf{k}}')]^* .\end{aligned} \tag{23}$$

Similar to what was found in (14), we see here that the ionization amplitude is again decomposed into a sum of transitions each involving the continuum wave function of the $e+M^+$ system belonging to a different IR of its symmetry group. On coupling

$$\{\mathcal{D}_{\mu_0\mu}^{1/2}(\omega_{u'})[\mathcal{D}_{\mu_0\mu'}^{1/2}(\omega_{u'})]^*\},\ \{[\mathcal{D}_{\nu\mu}^{1/2}(\omega)]^*\mathcal{D}_{\nu'\mu'}^{1/2}(\omega)\},\ \{[\mathcal{D}_{mn}^{l}(\omega)]^*\mathcal{D}_{m'n'}^{l'}(\omega)\},\ \{\mathcal{D}_{\lambda_r m_r}^{1}(\omega)[\mathcal{D}_{\lambda_r' m_r}^{1}(\omega)]^*\} ,$$

the spherical harmonics, and using the orthogonality relations[41] for 3-j symbols, one can write

$$\frac{d^2\sigma(m_r,\hat{\mathbf{u}}',\mu_0)}{d\omega\, d\hat{\mathbf{k}}'}=(-1)^{m_r+\mu_0}\frac{K}{W_b}\sum_{\mathrm{DS}}\sum_{L=0}^{2l_>}\sum_{M=-L}^{L}A_{LM}(\omega,\omega_{u'},m_r,\mu_0;k)Y_L^M(\hat{\mathbf{k}}') , \tag{24a}$$

where

$$\begin{aligned}A_{LM}&(\omega,\omega_{u'},m_r,\mu_0;k)\\ &=\sum_{N=-L}^{L}\sum_{\substack{p,\tau,h,l,m,\nu,\lambda_r,\\ p',\tau',h',l',m',\nu',\lambda_r'}}(-i)^{l-l'}e^{i(\sigma_l-\sigma_{l'})}(-1)^{m-\nu+\lambda_r}\left[\frac{(2l+1)(2l'+1)(2L+1)}{4\pi}\right]^{1/2}\begin{bmatrix} l & l' & L\\ 0 & 0 & 0\end{bmatrix}\\ &\quad\times\begin{bmatrix} l & l' & L\\ -m & m' & N\end{bmatrix}b_{hlm}^{p\tau}(b_{h'l'm'}^{p'\tau'})^*d_{hl\nu,b}^{p\tau}(\lambda_r)[d_{h'l'\nu',b}^{p'\tau'}(\lambda_r')]^*\\ &\quad\times\sum_{S=0}^{1}\sum_{M_S,N_S=-S}^{S}(2S+1)\begin{bmatrix} \frac{1}{2} & \frac{1}{2} & S\\ -\mu_0 & \mu_0 & 0\end{bmatrix}\begin{bmatrix} \frac{1}{2} & \frac{1}{2} & S\\ -\nu & \nu' & N_S\end{bmatrix}\mathcal{D}_{0M_S}^S(\omega_{u'})\\ &\quad\times\sum_{L_r=0}^{2}\sum_{N_r=-L_r}^{L_r}(2L_r+1)\begin{bmatrix} 1 & 1 & L_r\\ -m_r & m_r & 0\end{bmatrix}\begin{bmatrix} 1 & 1 & L_r\\ -\lambda_r & \lambda_r' & N_r\end{bmatrix}\end{aligned}$$

$$
\times \sum_{J=|L-S|}^{L+S} \sum_{M_J,N_J=-J}^{J} (2J+1) \begin{bmatrix} L & S & J \\ N & N_S & N_J \end{bmatrix} \begin{bmatrix} L & S & J \\ M & M_S & M_J \end{bmatrix}
$$

$$
\times \sum_{K=|J-L_r|}^{J+L_r} \sum_{N_K=-K}^{K} (2K+1) \begin{bmatrix} J & L_r & K \\ N_J & N_r & N_K \end{bmatrix} \begin{bmatrix} J & L_r & K \\ M_J & 0 & -M_J \end{bmatrix} [\mathcal{D}^K_{N_K,-M_J}(\omega)]^* \ . \tag{24b}
$$

The expression (24) is in its most general form and no approximations have been made in its derivation.

The angular distribution

$$
\frac{d^2\sigma(m_r)}{d\omega\, d\hat{\mathbf{k}}'} = \sum_{\mu_0} \frac{d^2\sigma(m_r,\hat{\mathbf{u}}',\mu_0)}{d\omega\, d\hat{\mathbf{k}}'} \ ,
$$

$$
\begin{aligned}
&= (-1)^{m_r} \frac{K}{W_b} \sum_{\mathrm{DS}} \sum_{L,M} \sum_{\substack{p,\tau,h,l,m,\lambda_r, \\ p',\tau',h',l',m',\lambda'_r}} (-i)^{l-l'} e^{i(\sigma_l-\sigma_{l'})} (-1)^{m+\lambda'_r} \left[\frac{(2l+1)(2l'+1)(2L+1)}{4\pi} \right]^{1/2} \\
&\qquad \times \begin{bmatrix} l & l' & L \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l & l' & L \\ -m & m' & m-m' \end{bmatrix} b^{p\tau}_{hlm} (b^{p'\tau'}_{h'l'm'})^* Y^M_L(\hat{\mathbf{k}}') \\
&\qquad \times \sum_{L_r K} (2L_r+1)(2K+1) \begin{bmatrix} 1 & 1 & L_r \\ -m_r & m_r & 0 \end{bmatrix} \begin{bmatrix} 1 & 1 & L_r \\ -\lambda_r & \lambda'_r & \lambda_r-\lambda'_r \end{bmatrix} \\
&\qquad \times \begin{bmatrix} L & L_r & K \\ m-m' & \lambda'_r-\lambda_r & Q \end{bmatrix} \begin{bmatrix} L & L_r & K \\ M & 0 & -M \end{bmatrix} \mathcal{D}^K_{Q,-M}(\omega) \\
&\qquad \times \sum_{\nu} d^{p\tau}_{hl\nu,b}(\lambda_r) [d^{p'\tau'}_{h'l'\nu,b}(\lambda'_r)]^*
\end{aligned} \tag{25}
$$

of spin-unresolved electrons ejected by photoionization in an oriented polyatomic molecule in photon frame of reference is obtained by using (18). This result is the same as previously obtained in Eqs. (13) in Ref. 22.

On comparing (24) with (16) and (25) with (19), we find that angular distributions both for spin-resolved and spin-unresolved photoelectrons are much more complicated in a photon frame of reference. In addition to the coherent, infinite sums over (l,m), (l',m'), and (L,M) present in both (16) and (24), the latter contains six more ($|N| \le L,J,K$, $|M_J| \le J$, $|N_J| \le J$, $|K| \le K$) such sums. Similarly, in the case of spin-unresolved photoelectrons, the angular distribution (25) in the photon frame has one more infinite sum over K, in addition to those six (l,l',L,m,m',M) present in (19) for molecule frame of reference. One can therefore conclude that each term in the angular distribution of spin-resolved as well as spin-unresolved photoelectrons in a molecule frame of reference is equivalent to many terms present in a photon frame of reference whenever a molecular target with fixed orientation in space is being ionized. However the total number of ionization amplitudes in the two cases will remain the same because it depends upon the number of partial waves (i.e., l,l') considered to represent the photoelectron.

The total spin-detected photocurrent for ionization in a laboratory frame of reference is obtained by substituting (24) in (20):

$$
\begin{aligned}
\frac{d\sigma(m_r,\hat{\mathbf{u}}',\mu_0)}{d\omega} &= (-1)^{m_r+\mu_0} \frac{K}{W_b} \sum_{\mathrm{DS}} \sum_{\substack{p,\tau,h,l \\ \nu,\nu',\lambda_r,\lambda'_r}} (-1)^{\lambda_r-\nu} d^{p\tau}_{nl\nu,b}(\lambda_r) [d^{p\tau}_{hl\nu',b}(\lambda'_r)]^* \\
&\qquad \times \sum_{S,M_S,N_S} (-1)^{M_S+N_S} (2S+1) \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ -\mu_0 & \mu_0 & 0 \end{bmatrix} \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & S \\ -\nu & \nu' & N_S \end{bmatrix} \\
&\qquad \times \mathcal{D}^S_{0M_S}(\omega_{u'}) \sum_{L_r,N_r} (2L_r+1) \begin{bmatrix} 1 & 1 & L_r \\ -m_r & m_r & 0 \end{bmatrix} \begin{bmatrix} 1 & 1 & L_r \\ -\lambda_r & \lambda'_r & N_r \end{bmatrix} \\
&\qquad \times \sum_{K,N_K} (2K+1) \begin{bmatrix} S & L_r & K \\ -N_S & N_r & N_K \end{bmatrix} \\
&\qquad \times \begin{bmatrix} S & L_r & K \\ -M_S & 0 & M_S \end{bmatrix} [\mathcal{D}^k_{N_K,M_S}(\omega)]^* \ .
\end{aligned} \tag{26}
$$

Similar to the result derived in Eq. (21), (26) too contains a single infinite sum over l only.

IV. IONIZATION IN MOLECULES WITH RANDOM ORIENTATION IN SPACE

The most direct procedure to obtain an expression for angular distribution of electrons ejected by photoionization in a freely rotating molecule is to average (24) over all possible orientations of the target in space. The differential ionization cross section

$$\frac{d\bar{\sigma}(m_r,\hat{\mathbf{u}}',\mu_0)}{d\mathbf{k}'}=\int\frac{d^2\sigma(m_r,\hat{\mathbf{u}}',\mu_0)}{d\omega\, d\hat{\mathbf{k}}'}\frac{1}{8\pi^2}d\omega \tag{27}$$

for photoelectrons propagating into the solid angle $d\hat{\mathbf{k}}'$ about $\hat{\mathbf{k}}'$ with the projection $\mu_0\hbar$ of their spin angular momentum along $\hat{\mathbf{u}}'$ in a photon frame of reference therefore becomes

$$\frac{d\bar{\sigma}(m_r,\hat{\mathbf{u}}',\mu_0)}{d\hat{\mathbf{k}}'}=(-1)^{m_r+\mu_0}\frac{K}{W_b}\sum_{\mathrm{DS}}\sum_{L,S,M}A_{LSM}(m_r,\hat{\mathbf{u}}',\mu_0;k)Y_L^M(\hat{\mathbf{k}}')Y_S^{-M}(\hat{\mathbf{u}}')\ , \tag{28a}$$

where

$$\begin{aligned}A_{LSM}(m_r,\hat{\mathbf{u}}',\mu_0;k)=&\sqrt{(2L+1)(2S+1)}\begin{bmatrix}\frac{1}{2} & \frac{1}{2} & S\\ -\mu_0 & \mu_0 & 0\end{bmatrix}\\ &\times\sum_{N}\sum_{\substack{p,\tau,h,l,m,\nu,\lambda_r,\\ p',\tau',h',l',m',\nu',\lambda_r'}}(-i)^{l-l'}e^{i(\sigma_l-\sigma_{l'})}(-1)^{m+\lambda_r'-\nu}\sqrt{(2l+1)(2l'+1)}\\ &\times\begin{bmatrix}l & l' & L\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}l & l' & L\\ -m & m' & N\end{bmatrix}b_{hlm}^{p\tau}(b_{h'l'm'}^{p'\tau'})^*d_{hl\nu,b}^{p\tau}(\lambda_r)[d_{h'l'\nu',b}^{p'\tau'}(\lambda_r')]^*\\ &\times\sum_{N_S}\begin{bmatrix}\frac{1}{2} & \frac{1}{2} & S\\ -\nu & \nu' & N_S\end{bmatrix}\sum_J(2J+1)\begin{bmatrix}1 & 1 & J\\ -m_r & m_r & 0\end{bmatrix}\begin{bmatrix}1 & 1 & J\\ -\lambda_r & \lambda_r' & \lambda_r-\lambda_r'\end{bmatrix}\\ &\times\begin{bmatrix}L & S & J\\ M & -M & 0\end{bmatrix}\begin{bmatrix}L & S & J\\ N & N_S & \lambda_r'-\lambda_r\end{bmatrix}\ .\end{aligned} \tag{28b}$$

If in an experimental arrangement on molecular photoionization, spin direction of ejected electrons is not detected, the corresponding angular distribution is given by

$$\frac{d\bar{\sigma}(m_r)}{d\hat{\mathbf{k}}'}=\sum_{\mu_0}\frac{d\bar{\sigma}(m_r,\hat{\mathbf{u}}',\mu_0)}{d\hat{\mathbf{k}}'}\ . \tag{29}$$

On substituting (28) in (29) and using the property (18), we obtain

$$\begin{aligned}\frac{d\bar{\sigma}(m_r)}{d\hat{\mathbf{k}}'}=&(-1)^{m_r}\frac{K}{4\pi W_b}\sum_{\mathrm{DS}}\sum_{L}\sum_{\substack{p,\tau,h,l,m,\lambda_r,\\ p',\tau',h',l',m',\lambda_r'}}(-i)^{l-l'}e^{i(\sigma_l-\sigma_{l'})}(-1)^{m+\lambda_r}(2L+1)\sqrt{(2l+1)(2l'+1)}\\ &\times\begin{bmatrix}l & l' & L\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}1 & 1 & L\\ -m_r & m_r & 0\end{bmatrix}\begin{bmatrix}1 & 1 & L\\ -\lambda_r & \lambda_r' & \lambda_r-\lambda_r'\end{bmatrix}\\ &\times\begin{bmatrix}l & l' & L\\ -m & m' & \lambda_r-\lambda_r'\end{bmatrix}b_{hlm}^{p\tau}(b_{h'l'm'}^{p'\tau'})^*P_L(\cos\theta')\sum_{\nu}d_{hl\nu,b}^{p\tau}(\lambda_r)[d_{h'l'\nu,b}^{p'\tau'}(\lambda_r')]^*\ .\end{aligned} \tag{30}$$

This expression agrees exactly with that derived by us in Eq. (14) in Ref. 22 for angular distribution of spin-unresolved electrons ejected by interaction of light with unoriented molecules in the $E1$ approximation.

V. ANGULAR MOMENTUM TRANSFER TREATMENT

In order to introduce the angular momentum transfer $\mathbf{j}_t$ defined by Eq. (2) in the ASRPES of polyatomic molecules, let us go back to distribution (23) in a photon frame of reference and couple the $\mathcal{D}$ functions present therein as follows:

$$\mathcal{D}^{1/2}_{\mu_0\mu}(\omega_{u'})[\mathcal{D}^{1/2}_{\mu_0\mu'}(\omega_{u'})]^* = (-1)^{\mu_0-\mu}\sum_{S,M_S}\sqrt{4\pi(2S+1)}\begin{bmatrix}\frac{1}{2} & \frac{1}{2} & S\\ -\mu_0 & \mu_0 & 0\end{bmatrix}\begin{bmatrix}\frac{1}{2} & \frac{1}{2} & S\\ -\mu & \mu' & M_S\end{bmatrix}Y_S^{M_S}(\hat{\mathbf{u}}'), \tag{31a}$$

$$\mathcal{D}^1_{\lambda_r m_r}(\omega)\{[\mathcal{D}^l_{mn}(\omega)]^*[\mathcal{D}^{1/2}_{\nu\mu}(\omega)]^*\} = \sum_{\substack{j,m_j,n_j,\\ j_t,m_1,m_2}}(-1)^{2(m_j-n_j)}(2j+1)(2j_t+1)\begin{bmatrix}l & \frac{1}{2} & j\\ -m & -\nu & m_j\end{bmatrix}$$
$$\times\begin{bmatrix}l & \frac{1}{2} & j\\ -n & -\mu & n_j\end{bmatrix}\begin{bmatrix}1 & j & j_t\\ \lambda_r & -m_j & m_1\end{bmatrix}\begin{bmatrix}1 & j & j_t\\ m_r & -n_j & m_2\end{bmatrix}[\mathcal{D}^{j_t}_{m_1m_2}(\omega)]^*, \tag{31b}$$

and

$$[\mathcal{D}^1_{\lambda_r' m_r}(\omega)]^*[\mathcal{D}^{l'}_{m'n'}(\omega)\mathcal{D}^{1/2}_{\nu'\mu'}(\omega)] = \sum_{\substack{j',m_{j'},n_{j'},\\ j_t',m_1',m_2'}}(-1)^{2(m_{j'}-n_{j'})}(2j'+1)(2j_t'+1)\begin{bmatrix}l' & \frac{1}{2} & j'\\ -m' & -\nu' & m_{j'}\end{bmatrix}$$
$$\times\begin{bmatrix}l' & \frac{1}{2} & j'\\ -n' & -\mu' & n_{j'}\end{bmatrix}\begin{bmatrix}1 & j' & j_t'\\ \lambda_r' & -m_{j'} & m_1'\end{bmatrix}\begin{bmatrix}1 & j' & j_t'\\ m_r & -n_{j'} & m_2'\end{bmatrix}\mathcal{D}^{j_t'}_{m_1'm_2'}(\omega). \tag{31c}$$

On substituting (31) and using the coupling rule[41] for spherical harmonics, expression (23) for angular distribution of electrons ejected into the solid angle $d\hat{\mathbf{k}}'$ about the direction of propagation $\hat{\mathbf{k}}'$ and with the spin component $\mu_0\hbar$ along the direction $\hat{\mathbf{u}}'$ by photoionization in a molecule with fixed orientation ω in space becomes

$$\frac{d^2\sigma(m_r,\hat{\mathbf{u}}',\mu_0)}{d\omega\, d\hat{\mathbf{k}}'} = (-1)^{1/2+\mu_0}\frac{K}{W_b}$$
$$\times\sum_{\mathrm{DS}}\sum_{\substack{p,\tau,h,l,m,\nu,\lambda_r,\\ p',\tau',h',l',m',\nu',\lambda_r'}}\sum_{\substack{L,S,J,\\ M_L,M_S,M_J}}(-i)^{l-l'}e^{i(\sigma_l-\sigma_{l'})}$$
$$\times(2J+1)\sqrt{(2l+1)(2l'+1)(2L+1)(2S+1)}\begin{bmatrix}l & l' & L\\ 0 & 0 & 0\end{bmatrix}$$
$$\times\begin{bmatrix}\frac{1}{2} & \frac{1}{2} & S\\ -\mu_0 & \mu_0 & 0\end{bmatrix}\begin{bmatrix}L & S & J\\ M_L & M_S & M_J\end{bmatrix}\begin{Bmatrix}l & \frac{1}{2} & j\\ l' & \frac{1}{2} & j'\\ L & S & J\end{Bmatrix}$$
$$\times b^{p\tau}_{hlm}(b^{p'\tau'}_{h'l'm'})^* d^{p\tau}_{hl\nu,b}(\lambda_r)[d^{p'\tau'}_{h'l'\nu',b}(\lambda_r')]^* Y_S^{M_S}(\hat{\mathbf{u}}')Y_L^{M_L}(\hat{\mathbf{k}}')$$
$$\times\sum_{\substack{j,m_j,n_j\\ j',m_{j'},n_{j'}}}\sum_{\substack{j_t,m_1,m_2\\ j_t',m_1',m_2'}}(-1)^{l'+j'+2(m_j+m_{j'}-n_{j'})-3n_j}$$
$$\times(2j+1)(2j'+1)(2j_t+1)(2j_t'+1)\begin{bmatrix}l & \frac{1}{2} & j\\ -m & -\nu & m_j\end{bmatrix}\begin{bmatrix}1 & j & j_t\\ \lambda_r & -m_j & m_1\end{bmatrix}$$
$$\times\begin{bmatrix}l' & \frac{1}{2} & j'\\ -m' & -\nu' & m_{j'}\end{bmatrix}\begin{bmatrix}1 & j' & j_t'\\ \lambda_r' & -m_{j'} & m_1'\end{bmatrix}\begin{bmatrix}1 & j & j_t\\ m_r & -n_j & m_2\end{bmatrix}$$
$$\times\begin{bmatrix}1 & j' & j_t'\\ m_r & -n_{j'} & m_2'\end{bmatrix}\begin{bmatrix}j & j' & J\\ n_j & -n_{j'} & M_J\end{bmatrix}[\mathcal{D}^{j_t}_{m_1m_2}(\omega)]^*\mathcal{D}^{j_t'}_{m_1'm_2'}(\omega). \tag{32}$$

This result is obtained by using an identity[45] which expresses a sum over four 3-j symbols in terms of the sum of a product of two 3-j symbols and one 9-j symbol.

In order to obtain the angular distribution of spin-polarized photoelectrons for ionization in randomly oriented molecules, we substitute (32) in (27) and use orthogonality of $\mathcal{D}$ functions.[41] One finds, after making some additional simplications,

$$\frac{d\bar{\sigma}(m_r,\hat{\mathbf{u}}',\mu_0)}{d\hat{\mathbf{k}}'}=(-1)^{1/2+\mu_0+m_r}\frac{K}{W_b}\sum_{\mathrm{DS}}\sum_{L,S,M}A_{LSM}(m_r,\hat{\mathbf{u}}',\mu_0;k)Y_L^M(\hat{\mathbf{k}}')Y_S^{-M}(\hat{\mathbf{u}}') \tag{33a}$$

with

$$A_{LSM}(m_r,\hat{\mathbf{u}}',\mu_0;k)=\sqrt{(2L+1)(2S+1)}\begin{bmatrix}\frac{1}{2} & \frac{1}{2} & S\\ -\mu_0 & \mu_0 & 0\end{bmatrix}$$

$$\times\sum_{\substack{l,l',j,j',\\ j_t,m_t}}(-1)^{l'+j'+j_t}(2j_t+1)\begin{bmatrix}l & l' & L\\ 0 & 0 & 0\end{bmatrix}d_{l,1/2,j;b}(j_tm_t)[d_{l',1/2,j';b}(j_tm_t)]^*$$

$$\times\sum_J(2J+1)\begin{bmatrix}1 & 1 & J\\ -m_r & m_r & 0\end{bmatrix}\begin{bmatrix}L & S & J\\ M & -M & 0\end{bmatrix}\begin{Bmatrix}1 & 1 & J\\ j & j' & j_t\end{Bmatrix}\begin{Bmatrix}l & \frac{1}{2} & j\\ l' & \frac{1}{2} & j'\\ L & S & J\end{Bmatrix}. \tag{33b}$$

Here we have introduced a new set of amplitudes,

$$d_{l,1/2,j;b}(j_tm_t)=(-i)^le^{i\sigma_l}(2j+1)\sqrt{2l+1}\sum_{\substack{p,\tau,h,m,\\ \nu,\lambda_r,m_j}}\begin{bmatrix}l & \frac{1}{2} & j\\ -m & -\nu & m_j\end{bmatrix}\begin{bmatrix}1 & j & j_t\\ \lambda_r & -m_j & m_t\end{bmatrix}b_{hlm}^{p\tau}d_{hl\nu,b}^{p\tau}(\lambda_r) \tag{34}$$

called "reduced" amplitudes. The continuum channels in these new amplitudes are characterized by j_t, the angular momentum transferred [according to the definition (2)] from the photon to the ejected electron which is observed with its spin, and by the projection $-j_t \leq m_t \leq j_t$ along the molecular axis.

The angular distribution (33) is much simpler than (28) derived in Sec. IV. The 12 sums over the variables p, τ, h, m, ν, λ_r, p', τ', h', m', ν', and λ_r' along with their cross terms, which are present in the angular distribution (28) for photoionization in unoriented molecules, have been replaced in (33) by a double sum over j and j' and by two "incoherent" sums over j_t and m_t. The 12 "coherent" sums which are absent in (33) are actually hidden in the definition (34) of the reduced amplitudes.

Thus, unlike the expression derived by Klar,[34] the spin-resolved photoelectron angular distribution (33) for ionization in randomly oriented targets does not contain interference terms $j_t \neq j_t'$. This comes about because we have introduced through Eq. (2) in this paper a different (and probably correct) angular momentum exchanged between the unobserved initial and final angular momenta than that defined by Eq. (1) used by Klar.[34]

The presence of a sum in (33) over the projection m_t of j_t along the molecular axis, on the other hand, is a manifestation of the fact that the axial angular momentum for nonlinear molecules, unlike for linear systems, is not a conserved quantity. A similar situation has already been found by us[22,24] in angular distribution of spin-unpolarized electrons ejected by photoionization in freely rotating nonlinear molecules. On the basis of the previous study,[24] one can readily conclude that the reduced amplitude introduced in (34) will be extremely useful in analyzing the contributions of various dipole matrix elements to ASRPES of polyatomic molecules according to parity-favored and -unfavored transitions. Such an investigation will be the subject of one of our future communications.[46]

VI. ANALYSIS OF THE PHOTOELECTRON ANGULAR DISTRIBUTION

In order to be able to study the structure of the angular distribution and use it further below, it is necessary to simplify the expressions obtained in Secs. III–V and make them as transparent as possible. For simplicity and ease in analysis, we shall henceforth discuss in this paper photoionization in molecules with only random orientation in space.

In both of the expressions (28) and (33) we always have $S=0,1$ and $J=0,1,2$. Consequently, the allowed values of L are 0, 1, 2, and 3. However, when the summation over degenerate states of both the preionization target M and postionization residue M^+ is carried out, the contributions of the odd L (i.e., 1 and 3) vanish identically. After using the Racah algebra, one can show that each of the two expressions (28) and (33) can be written in the following form:

$$
\begin{aligned}
\frac{d\bar{\sigma}(m_r,\hat{\mathbf{u}}',\mu_0)}{d\hat{\mathbf{k}}'} = \frac{\bar{\sigma}}{8\pi}\{ & 1+\tfrac{1}{2}(2-3m_r^2)\bar{\beta}P_2(\cos\theta')-2m_r\mu_0\bar{\gamma}\cos\theta_{u'} \\
& +2m_r\mu_0\bar{\delta}[P_2(\cos\theta')\cos\theta_{u'}+\tfrac{1}{2}P_2^1(\cos\theta')\sin\theta_{u'}\cos(\phi_{u'}-\phi')] \\
& +\tfrac{2}{3}(3m_r^2-2)\mu_0\bar{\xi}P_2^1(\cos\theta')\sin\theta_{u'}\sin(\phi_{u'}-\phi')\} \qquad (35a)
\end{aligned}
$$

$$
\begin{aligned}
= \frac{\bar{\sigma}}{8\pi}\{ & 1+\tfrac{1}{4}(2-3m_r^2)\bar{\beta}(3\cos^2\theta'-1)-2m_r\mu_0\bar{\gamma}\cos\theta_{u'} \\
& +m_r\mu_0\bar{\delta}[(3\cos^2\theta'-1)\cos\theta_{u'}+\tfrac{3}{2}\sin2\theta'\sin\theta_{u'}\cos(\phi_{u'}-\phi')] \\
& +(3m_r^2-2)\mu_0\bar{\xi}\sin2\theta'\sin\theta_{u'}\sin(\phi_{u'}-\phi')\}\ . \qquad (35b)
\end{aligned}
$$

Here, P_2 and P_2^1 are the associated Legendre polynomials of second order but of degrees zero and one, respectively. The five parameters $\bar{\alpha}$, $\bar{\beta}$, $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\xi}$ present in the Eq. (35) are as follows:

$$
\bar{\sigma}=\frac{K}{3W_b}\sum_{\mathrm{DS}}\sum_{p,\tau,h,l,\nu,\lambda_r}|d^{p\tau}_{hl\nu,b}(\lambda_r)|^2 \qquad (36a)
$$

$$
=\frac{K}{3W_b}\sum_{\mathrm{DS}}\sum_{l,j,j_t,m_t}(2j_t+1)[(2l+1)(2j+1)]^{-1}|d_{l,1/2,j;b}(j_tm_t)|^2\ , \qquad (36b)
$$

$$
\begin{aligned}
\bar{\beta}= & \frac{2}{\bar{\sigma}}\left[\frac{5}{6}\right]^{1/2}\frac{K}{W_b}\sum_{\mathrm{DS}}\sum_{\substack{p,\tau,h,l,m,\lambda_r,\\ p',\tau',h',l',m',\lambda_r'}}\sum_{\nu}(-i)^{l-l'}e^{i(\sigma_l-\sigma_{l'})}(-1)^{m+\lambda_r}\sqrt{(2l+1)(2l'+1)}\begin{bmatrix} l & l' & 2\\ 0 & 0 & 0\end{bmatrix} \\
& \times\begin{bmatrix} l & l' & 2\\ -m & m' & N\end{bmatrix}\begin{bmatrix} 1 & 1 & 2\\ -\lambda_r & \lambda_r' & N\end{bmatrix}b^{p\tau}_{hlm}(b^{p'\tau'}_{h'l'm'})^{*}d^{p\tau}_{dl\nu,b}(\lambda_r)[d^{p'\tau'}_{h'l'\nu,b}(\lambda_r')]^{*} \qquad (37a)
\end{aligned}
$$

$$
\begin{aligned}
= & -\frac{2}{\bar{\sigma}}\left[-\frac{5}{6}\right]^{1/2}\frac{K}{W_b}\sum_{\mathrm{DS}}\sum_{\substack{l,l',j,j',\\ j_t,m_t}}(-1)^{l+l'+j_t}(2j_t+1)\begin{bmatrix} l & l' & 2\\ 0 & 0 & 0\end{bmatrix}\begin{Bmatrix} 1 & 1 & 2\\ j & j' & j_t\end{Bmatrix}\begin{Bmatrix} l & l' & 2\\ j' & j & \frac{1}{2}\end{Bmatrix} \\
& \times d_{l,1/2,j;b}(j_tm_t)[d_{l',1/2,j';b}(j_tm_t)]^{*}\ , \qquad (37b)
\end{aligned}
$$

$$
\bar{\gamma}=-(-1)^{1/2}\frac{K}{\bar{\sigma}W_b}\sum_{\mathrm{DS}}\sum_{p,\tau,h,l}\sum_{\substack{\lambda_r,\lambda_r',\\ \nu,\nu'}}(-1)^{\lambda_r-\nu}\begin{bmatrix} 1 & 1 & 1\\ -\lambda_r & \lambda_r' & N\end{bmatrix}\begin{bmatrix} \frac{1}{2} & \frac{1}{2} & 1\\ -\nu & \nu' & N\end{bmatrix}d^{p\tau}_{hl\nu,b}(\lambda_r)[d^{p\tau}_{hl\nu',b}(\lambda_r')]^{*}\ , \qquad (38a)
$$

$$
\begin{aligned}
= & (-1)^{1/2}\frac{K}{\bar{\sigma}W_b}\sum_{\mathrm{DS}}\sum_{l,j,j',j_t,m_t}(-1)^{l+j+j'+j_t} \\
& \times(2j_t+1)(2l+1)^{-1}\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1\\ j & j' & l\end{Bmatrix}\begin{Bmatrix} 1 & 1 & 1\\ j & j' & j_t\end{Bmatrix}d_{l,1/2,j;b}(j_tm_t)[d_{l,1/2,j';b}(j_tm_t)]^{*}\ , \qquad (38b)
\end{aligned}
$$

$$
\begin{aligned}
\bar{\delta}= & \sqrt{-30}\frac{K}{\bar{\sigma}W_b} \\
& \times\sum_{\mathrm{DS}}\sum_{\substack{p,\tau,h,l,m,\nu,\lambda_r,\\ p',\tau',h',l',m',\nu',\lambda_r'}}(-i)^{l-l'}e^{i(\sigma_l-\sigma_{l'})}(-1)^{m+\lambda_r'-\nu}\sqrt{(2l+1)(2l'+1)}\begin{bmatrix} l & l' & 2\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix} 1 & 1 & 1\\ -\lambda_r & \lambda_r' & N\end{bmatrix} \\
& \times b^{p\tau}_{hlm}(b^{p'\tau'}_{h'l'm'})^{*}d^{p\tau}_{hl\nu,b}(\lambda_r)[d^{p'\tau'}_{h'l'\nu',b}(\lambda_r')]^{*} \\
& \times\sum_{M}\begin{bmatrix} l & l' & 2\\ -m & m' & M\end{bmatrix}\begin{bmatrix} \frac{1}{2} & \frac{1}{2} & 1\\ -\nu & \nu' & N-M\end{bmatrix}\begin{bmatrix} 2 & 1 & 1\\ M & N-M & -N\end{bmatrix}, \qquad (39a)
\end{aligned}
$$

$$= -\sqrt{30}\frac{K}{\bar{\sigma} W_b} \sum_{\mathrm{DS}} \sum_{\substack{l,l',j,j',\\ j_t,m_t}} (-1)^{l'+j'+j_t}(2j_t+1) \begin{bmatrix} l & l' & 2 \\ 0 & 0 & 0 \end{bmatrix} \begin{Bmatrix} 1 & 1 & 1 \\ j & j' & j_t \end{Bmatrix} \begin{Bmatrix} l & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ 2 & 1 & 1 \end{Bmatrix}$$

$$\times d_{l,!/2,j;b}(j_t m_t)[d_{l',1/2,j';b}(j_t m_t)]^* \;, \tag{39b}$$

$$\bar{\xi} = -i5\sqrt{-3/2}\frac{K}{\bar{\sigma} W_b} \sum_{\mathrm{DS}} \sum_{\substack{p,\tau,h,l,m,\nu,\lambda_r,\\ p',\tau',h',l',m',\nu',\lambda_r'}} (-i)^{l-l'} e^{i(\sigma_l - \sigma_{l'})}(-1)^{m+\lambda_r'-\nu}\sqrt{(2l+1)(2l'+1)}$$

$$\times \begin{bmatrix} l & l' & 2 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 & 1 & 2 \\ -\lambda_r & \lambda_r' & N \end{bmatrix} b_{hlm}^{p\tau}(b_{h'l'm'}^{p'\tau'})^* d_{hl\nu,b}^{p\tau}(\lambda_r)[d_{h'l'\nu',b}^{p'\tau'}(\lambda_r')]^*$$

$$\times \sum_{M} \begin{bmatrix} l & l' & 2 \\ -m & m' & M \end{bmatrix} \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ -\nu & \nu' & N-M \end{bmatrix} \begin{bmatrix} 2 & 1 & 2 \\ M & N-M & -N \end{bmatrix} , \tag{40a}$$

$$= i5\sqrt{3/2}\frac{K}{\bar{\sigma} W_b} \sum_{\mathrm{DS}} \sum_{\substack{l,l',j,j',\\ j_t,m_t}} (-1)^{l'+j'+j_t}(2j_t+1) \begin{bmatrix} l & l' & 2 \\ 0 & 0 & 0 \end{bmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ j & j' & j_t \end{Bmatrix} \begin{Bmatrix} l & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ 2 & 1 & 2 \end{Bmatrix} d_{l,1/2,j;b}(j_t m_t)[d_{l',1/2,j';b}(j_t m_t)]^* \;. \tag{40b}$$

All the five expressions (36)–(40) are exact and in their most general forms. These can be used to study ASRPES in $E1$ approximation of unoriented molecules of any symmetry belonging to one of the 32 point groups. Also, these expressions are applicable to photoionization by linearly ($m_r=0$), and left ($m_r=+1$) and right ($m_r=-1$) circularly polarized incident light. In the case of unpolarized radiation, one needs to average (35) over $m_r=\pm 1$. We also note from the relation (40b) that the parameter $\bar{\xi}$ will always be zero whenever $l=l'$ and $j=j'$. Because, in such cases, the 9-j symbol presented in this expression vanishes identically.[45] Only the interference terms $l \neq l'$ and/or $j \neq j'$ will therefore contribute to $\bar{\xi}$.

The differential cross section

$$\frac{d\bar{\sigma}(m_r)}{d\hat{\mathbf{k}}'} = \frac{\bar{\sigma}}{4\pi}[1+\tfrac{1}{2}(2-3m_r^2)\bar{\beta}P_2(\cos\theta')]$$

for photoionization in the absence of any spin detection of ejected electrons is obtained by substituting (35) in (29). This expression has the well-known form.[47] In the angular distribution (35) of the spin-polarized photoelectrons $\bar{\sigma}$ is therefore the integrated partial-photoionization cross section and $\bar{\beta}$ is the asymmetry parameter. The respective two expressions (36) and (37) for these quantities are same as derived by us earlier[22] in differential cross sections of spin-unresolved photoelectrons. $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\xi}$, on the other hand, are the three parameters needed to study the degree of spin polarization of photoelectrons.

Let us assume that the propagation vector $\mathbf{k}'(k,\theta',\phi')$ of the departing electron lies in the X'-Z' plane of our photon frame, i.e., X'-Z' is the scattering plane. The $0Y'$ axis is then perpendicular to this plane. We then obviously have $\hat{\mathbf{k}}'$ ($\theta'=\theta_p$, $\phi'=0$). If we take ($\theta_{u'}=\alpha$, $\phi_{u'}=\phi$) to be the spherical polar angles of the direction $\hat{\mathbf{u}}'$ of the spin quantization of the photoelectron, the distribution (35a) then assumes the following simple form for ionization by right circularly polarized ($m_r=-1$) light:

$$\frac{d\bar{\sigma}(m_r,\hat{\mathbf{u}}',\mu_0)}{d\hat{\mathbf{k}}'} = \frac{\bar{\sigma}}{8\pi}\{1-\tfrac{1}{2}\bar{\beta}P_2(\cos\theta_p)+\bar{\gamma}\cos\alpha-\bar{\delta}[P_2(\cos\theta p)\cos\alpha+\tfrac{1}{2}P_2^1(\cos\theta_p)\sin\alpha\cos\phi]+\tfrac{1}{3}\bar{\xi}P_2^1(\cos\theta_p)\sin\alpha\sin\phi\}$$

$$\text{for } m_r=-1, \quad \mu_0=+\tfrac{1}{2} \;.$$

The angular structure of this equation is exactly the same as given by Cherepkov[11] in Eq. (A1) in his paper on photoionization in unoriented linear molecules. However, the expressions (36)–(40) for the five parameters obtained in this paper are different from those given earlier by Cherepkov.[11] According to the discussion in Sec. I in this paper, the differences between the two cases stem from the facts that, unlike the previous derivations,[11–16] the present formulation (i) uses the symmetry group of the molecule to maximum possible extent, (ii) is applicable to photoionization in both linear and nonlinear targets, and (iii) takes full account of the anisotropic final-state interaction between the departing photoelectron and the residual molecular ion.

The other interesting and important feature of the results obtained herein is that the expressions (36b)–(40b) for the five parameters in terms of (j_t,m_t) are always much simpler compared to their counterpart formulas (36a)–(40a) which are not based on angular momentum transfer treatment. And also, unlike those formulas which are derived by Klar[34] for ASRPES studies in atomic targets, none of (36b)–(40b) contains more than one sum over j_t, so that the interference terms $j_t \neq j_t'$ are not present as well. It will therefore certainly be much easier to calculate $\bar\sigma$, $\bar\beta$, $\bar\gamma$, $\bar\delta$, and $\bar\xi$ using these expressions than otherwise. Relations (36b)–(40b) will further be useful in analyzing the contributions of parity-favored and parity-unfavored transitions to the five parameters $\bar\sigma$, $\bar\beta$, $\bar\gamma$, $\bar\delta$, and $\bar\xi$.[46]

The integrated partial cross section for spin-polarized photoelectrons is given by

$$\bar\sigma(m_r,\hat{\mathbf u}',\mu_0)=\int \frac{d\bar\sigma(m_r,\hat{\mathbf u}',\mu_0)}{d\hat{\mathbf k}'}\,d\hat{\mathbf k}' = \frac{\bar\sigma}{2}(1-2m_r\mu_0\bar\gamma\cos\theta_{u'}) \ . \tag{41}$$

It is therefore only $\bar\gamma$, out of the three spin parameters (38)–(40), which contributes to the spin-polarized total photocurrent.

VII. ANALYSIS OF THE DEGREE OF SPIN POLARIZATION

The degree of spin polarization of photoelectrons ejected with the propagation vector $\mathbf k'$, in the photon frame of reference by interaction with an atomic or molecular target of light whose state of polarization is specified by m_r is given by

$$P(m_r,\hat{\mathbf u}';\mathbf k') = \frac{\dfrac{d\bar\sigma(m_r,\hat{\mathbf u}',\mu_0=+\frac12)}{d\hat{\mathbf k}'}-\dfrac{d\bar\sigma(m_r,\hat{\mathbf u}',\mu_0=-\frac12)}{d\hat{\mathbf k}'}}{\dfrac{d\bar\sigma(m_r,\hat{\mathbf u}',\mu_0=+\frac12)}{d\hat{\mathbf k}'}+\dfrac{d\bar\sigma(m_r,\hat{\mathbf u}',\mu_0=-\frac12)}{d\hat{\mathbf k}'}} \ .$$

On substituting (35b), it becomes

$$\begin{aligned}P(m_r,\hat{\mathbf u}',\mathbf k')=\tfrac12\{&-2m_r\bar\gamma\cos\theta_{u'}+m_r\bar\delta[(3\cos^2\theta'-1)\cos\theta_{u'}+\tfrac32\sin2\theta'\sin\theta_{u'}\cos(\phi_{u'}-\phi')]\\&+(3m_r^2-2)\bar\xi\sin2\theta'\sin\theta_{u'}\sin(\phi_{u'}-\phi')\}[1+\tfrac12(2-3m_r^2)\bar\beta P_2(\cos\theta')]^{-1} \ .\end{aligned} \tag{42}$$

The degree of polarization for the total photocurrent can be obtained either by integrating (42) or directly from

$$P(m_r,\hat{\mathbf u}')=\frac{\bar\sigma(m_r,\hat{\mathbf u}',\mu_0=+\frac12)-\bar\sigma(m_r,\hat{\mathbf u}',\mu_0=-\frac12)}{\bar\sigma(m_r,\hat{\mathbf u}',\mu_0=+\frac12)+\bar\sigma(m_r,\hat{\mathbf u}',\mu_0=-\frac12)} \ .$$

Use of (41) shows

$$P(m_r,\hat{\mathbf u}')=-m_r\bar\gamma\cos\theta_{u'} \ , \tag{43}$$

i.e., the integrated photoionization cross section is spin polarized only for circularly polarized incident radiation.[5]

The degree of spin polarization of the angularly distributed photocurrent produced by interaction of linearly polarized radiation with an unoriented molecule is obtained by taking $m_r=0$ in (42),

$$P(m_r=0,\hat{\mathbf u}';\mathbf k')=-\bar\xi\frac{\sin2\theta'\sin\theta_{u'}\sin(\phi_{u'}-\phi')}{1+\bar\beta P_2(\cos\theta')} \ . \tag{44}$$

The maximum polarization in this case is obviously for $\theta_{u'}=\pi/2$ and $\phi_{u'}=\pi/2+\phi'$, i.e., $\hat{\mathbf u}'$ is perpendicular to the plane containing the $0Z'$ axis and the direction of propagation, i.e., the scattering plane, and photoelectrons are polarized transversely to the direction of propagation, denoted by $\hat{\mathbf u}'_{\mathrm{trans},\perp}$. Hence

$$P_{\max}(m_r=0;\mathbf k')=P(m_r=0,\hat{\mathbf u}'_{\mathrm{trans},\perp};\mathbf k') = -\bar\xi\frac{\sin2\theta'}{1+\bar\beta P_2(\cos\theta')} \ . \tag{45}$$

We also have from (44) that $P(m_r=0,\hat{\mathbf u}';\mathbf k')=0$ if (i) $\theta'=n\pi/2$, i.e., the propagation vector is either along $(n=0,2)$ or perpendicular $(n=1)$ to the polar axis which is along the electric vector in the linearly polarized incident light; (ii) $\theta_{u'}=n\pi$, i.e., $\hat{\mathbf u}'$ is along $(n=0,1)$ the electric vector; (iii) $\phi_{u'}=\phi'+n\pi$, i.e., $\hat{\mathbf u}'$ lies $(n=0,1,2)$ in the scattering plane.

The degree of spin polarization

$$\begin{aligned}P(m_r=\pm1,\hat{\mathbf u}';\mathbf k')=\tfrac12\{&-2m_r\bar\gamma\cos\theta_{u'}+m_r\bar\delta[(3\cos^2\theta'-1)\cos\theta_{u'}+\tfrac32\sin2\theta'\sin\theta_{u'}\cos(\phi_{u'}-\phi')]\\&+\bar\xi\sin2\theta'\sin\theta_{u'}\sin(\phi_{u'}-\phi')\}/[1-\tfrac12\bar\beta P_2(\cos\theta')]\end{aligned} \tag{46}$$

of differential cross section for photoionization by circularly polarized light is again obtained by the relation (42). Let us consider the following cases discussed by Klar.[48]

(a) $\theta_{u'}=\theta'$ and $\phi_{u'}=\phi'$, i.e., $\hat{\mathbf{u}}'$ is parallel to $\hat{\mathbf{k}}'$. Therefore, for longitudinally polarized photoelectrons,

$$P(m_r=\pm 1,\hat{\mathbf{u}}'_{\text{long}};\mathbf{k}')=m_r\frac{(\bar{\delta}-\bar{\gamma})\cos\theta'}{1-\frac{1}{2}\bar{\beta}P_2(\cos\theta')} . \qquad (47)$$

(b) $\theta_{u'}=\pi/2$ and $\phi_{u'}=\phi'+\pi/2$, i.e., $\hat{\mathbf{u}}'$ is perpendicular to the scattering plane and photoelectrons are polarized transversely to the direction of propagation,

$$P(m_r=\pm 1,\hat{\mathbf{u}}'_{\text{trans},\perp};\mathbf{k}')=\frac{1}{2}\frac{\bar{\xi}\sin2\theta'}{1-\frac{1}{2}\bar{\beta}P_2(\cos\theta')} . \qquad (48)$$

(c) $\theta_{u'}=\theta'+\pi/2$ and $\phi_{u'}=\phi'$ for $0\le\theta'\le\pi/2$ or $\theta_{u'}=3\pi/2-\theta'$ and $\phi_{u'}=\phi'+\pi$ for $\pi/2\le\theta'\le\pi$, i.e., $\hat{\mathbf{u}}'$ is parallel to the scattering plane but the photoelectrons are polarized transversely to their direction of propagation,

$$P(m_r,\hat{\mathbf{u}}'_{\text{trans},\parallel};\mathbf{k}')=m_r\frac{(2\bar{\gamma}+\bar{\delta})\sin\theta'}{2[1-\frac{1}{2}\bar{\beta}P_2(\cos\theta')]} . \qquad (49)$$

Finally, the degree of spin polarization of photoelectrons produced by unpolarized light is given by

$$\begin{aligned}P^{\text{unp}}(\hat{\mathbf{u}}';\mathbf{k})&=\tfrac{1}{2}[P(m_r=+1,\hat{\mathbf{u}}';\mathbf{k}')+P(m_r=-1,\hat{\mathbf{u}}';\mathbf{k}')]\\&=\tfrac{1}{2}\bar{\xi}\frac{\sin2\theta'\sin\theta_{u'}\sin(\phi_{u'}-\phi')}{1-\frac{1}{2}\bar{\beta}P_2(\cos\theta')} . \qquad (50)\end{aligned}$$

Therefore, analogous to Eq. (45) for photoionization by linearly polarized light, we have

$$\begin{aligned}P^{\text{unp}}_{\max}(\hat{\mathbf{u}}';\mathbf{k}')&=P^{\text{unp}}(\hat{\mathbf{u}}'_{\text{trans},\perp};\mathbf{k}')\\&=\tfrac{1}{2}\bar{\xi}\frac{\sin2\theta'}{1-\frac{1}{2}\bar{\beta}P_2(\cos\theta')} . \qquad (51)\end{aligned}$$

[The polar axis of the photon frame is along the direction of incidence of the unpolarized (or circularly polarized) light.] Thus, in view of Eqs. (50) and (51), the discussion given after Eqs. (44) and (45) for linearly polarized incident beam is also applicable to photoionization by unpolarized light.

VIII. CONCLUSION

In this paper we have developed a multichannel theory for ASRPES of molecules with fixed as well as random orientation in space. The formulation is based on an application of the group-theoretical methods to describe the symmetry properties of the molecular targets. Consequently, the expressions derived herein are not only exact and most general, but also are in their simplest possible forms. The theory is applicable to ASRPES studies in any molecule, linear or nonlinear, which belongs to one of the 32 points groups. This formulation takes properly into account also the anisotropic final-state interaction between the departing electron and the residual molecular ion. For oriented targets, the expressions for photoelectron angular distribution are obtained for ionization in both the molecule and photon frame of reference.

Further, the angular momentum transfer treatment of the desired process is also presented in this paper. A new coupling scheme, which is different from those used hitherto by other workers, is introduced to define the angular momentum $\mathbf{j}_t$ transferred from the incident photon to the ejected electron. This new scheme not only considerably simplifies the resulting expressions both for photoelectron angular distribution and spin-polarization parameters, but also eliminates the coherence terms (i.e., the interference terms with $j_t\neq j_t'$) which were present in earlier angular momentum transfer treatment of the ASRPES studies in randomly oriented targets.

A detailed application of the theory developed in this paper to angle- and spin-resolved photoionization in unoriented T_d molecules is presented in the succeeding article.[37] The three spin-polarization parameters $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\xi}$ are calculated for ionization in $4a_1^2$, $6a_1^2$, and $7a_1^2$ orbitals of CF_4, CCl_4, and $SiCl_4$, respectively.

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