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Photoelectron spectroscopic studies of polyatomic molecules: Spin-polarized electrons from oriented T_d molecules

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This paper presents a theoretical study of angular distribution of spin-resolved electrons ejected by interaction of light in the nonrelativistic, electric dipole approximation with nonlinear molecules oriented in space. A theory, formulated in an earlier paper [N. Chandra, Phys. Rev. A **40**, 752 (1989)] by taking full account of the group-theoretical transformation properties of a molecular target, is used to develop explicit expressions for the four parameters [namely, the spin-unresolved differential cross section $d^2\sigma(m_r)/d\hat{\mathbf{k}}d\omega$ for photoionization and the three polarization parameters $\chi(m_r,\mathbf{k},\omega)$, $\kappa(m_r,\mathbf{k},\omega)$, and $\zeta(m_r,\mathbf{k},\omega)$ that depend upon the state of polarization m_r for the ionizing radiation, propagation vector $\mathbf{k}$, and the orientation of the molecule in space] needed to describe the angularly distributed, spin-polarized photocurrent from linear as well as nonlinear molecules of any symmetry corresponding to one of the 32 point groups, oriented in space in their gaseous phase or on liquid (solid) surfaces. These formulas have been applied to angle- and spin-resolved photoelectron spectroscopy of the a_1 orbital in those molecules that transform like the T_d point symmetry group. The spin polarization of photoelectrons in this case is due directly to the spin-orbit interaction in the molecular continua. Detailed expressions for the four parameters with the electric vector in the radiation beam both parallel and perpendicular to the fixed axis of the oriented molecule are derived, probably in their simplest possible form, using the concepts of the extended (or spin-double) group. The properties of these parameters, which are influenced, *inter alia*, also by the spin-orbit interaction, are analyzed. Such angle- and spin-resolved studies of photoionization in oriented molecules will therefore provide more stringent tests for theoretical models, probes into the effects of target orientation on photoionization dynamics, and a measure of the influence of the spin-orbit interaction on the continuum part of the spectrum. The procedure adopted and the formulation presented herein set a methodology and a framework for the analysis of the measurements and calculations of angle- and spin-resolved photoelectron spectra of those polyatomics in general, and T_d molecules, in particular, which have a fixed orientation in space. The specific examples considered in this paper are photoionization in $4a_1^2$, $6a_1^2$, and $7a_1^2$ orbitals of oriented CF_4, CCl_4, and $SiCl_4$, respectively. Without performing any dynamical calculations, the variations of various parameters with respect to the energy of the incident radiation and to the phases involved have semiempirically been studied in detail for two different orientations of the axis of the fixed molecule. This study has helped also in predicting the values of the polarization parameters in the energy range of the Cooper minimum for angle- and spin-resolved $CCl_4(6a_1^2)^{-1}$ and $SiCl_4(7a_1^2)^{-1}$ photoelectron spectra in oriented molecular targets.

I. INTRODUCTION

Recent experimental[1-4] as well as theoretical[5-11(a)] investigations on photoionization of freely rotating linear and nonlinear molecules have shown that, similar to the case of atoms,[11] one does not need targets with oriented spins in order to produce spin-polarized photoelectrons. This spin polarization of molecular photoelectrons, ejected by unpolarized, linearly, or circularly polarized light in the nonrelativistic, electric dipole ($E1$) approximation is due to the influence of the spin-orbit interaction (SOI) on the ground, ionic, and/or continuum states of the target. Because the degree of spin polarization of the photocurrent depends also on its direction of propagation, the photoemission experiments measuring the spin polarization should therefore be angle resolved as well. Angular distributions of ejected electrons are particularly sensitive probes of the photoionization dynamics as they contain, among other things, information on the phase of the ionization matrix elements and a dependence on the various possible continuum waves that describe a photoelectron.

Furthermore, the angular distribution of electrons ejected in photoionization of molecules oriented[12] in space (e.g., in a beam by a suitable combination of electric and/or magnetic fields,[13-15] or adsorbed onto a surface in solid phase[16]) is potentially a much richer source of information[17] because it will not involve an average over all possible orientations of the target, usually done while photoionizing freely rotating systems. The angle-resolved photoelectron spectroscopy (ARPES) of free, oriented molecules has been performed theoretically for linear diatomics,[18-22] nonlinear polyatomics,[23-25] and for CH_3I experimentally.[15] The recent investigations have further shown that the circular dichroism exists in photoelectron angular distribution from oriented molecules within the $E1$ approximation even in the absence of any SOI.[6(c),26-29]

In this paper we present, results of a theoretical study of angle- and spin-resolved photoelectron spectroscopy (ASRPES) in unpolarized, free, oriented molecules. The present study (whose short accounts have earlier been reported elsewhere[30,31]) is based on the general multichannel theory for ASRPES of unpolarized, oriented, linear and nonlinear molecules developed in Ref. 9 (hereafter referred to as I). In this communication we show how the application of this theory,[9] along with the concepts of extended point (spin-double) groups,[32] simplify a formidable problem to the maximum possible extent so that the whole physical process becomes as transparent as possible. This paper therefore develops a methodology, by means of an example of photoionization in the a_1 orbital in T_d molecules, for studying ASRPES of nonlinear molecular systems with a fixed orientation in space using group-theoretical techniques. Cherepkov[11(a)] and Cherepkov and Kuznetsov[6(b),6(c)] have also derived expressions for angular distribution of photoelectrons ejected from oriented molecules of relatively low symmetry. It has already been discussed in detail elsewhere[9,29,31] that their treatment is very different in several respects from that given in I and used in the present work.

The general theory for ASRPES of oriented molecules is first briefly reviewed and then adapted to the present investigation in the next section. Section III describes an application of this approach to photoionization in the highest a_1 valence orbitals of CF_4, CCl_4, and $SiCl_4$ molecules, all oriented in space and belonging to the T_d point group. The two particular cases considered in this paper correspond to photoionization by photon beams with electric vector parallel and perpendicular to the fixed axis of the highest symmetry (also called the molecular axis) in a linear or nonlinear target oriented in space. Finally, the conclusions of this study are presented in Sec. IV.

II. THEORY FOR ASRPES OF ORIENTED MOLECULES

The angular distribution of spin-resolved electrons ejected by interaction of light in nonrelativistic, $E1$ approximation with an oriented, but otherwise unpolarized, molecule is given by[30,31]

$$\frac{d^2\sigma(m_r,\hat{\mathbf{u}},\nu_0)}{d\hat{\mathbf{k}}d\omega}=\frac{1}{2}\frac{d^2\sigma(m_r)}{d\hat{\mathbf{k}}d\omega}\{1+2\nu_0[\chi(m_r,\mathbf{k},\omega)\sin\theta_u\cos\phi_u+\kappa(m_r,\mathbf{k},\omega)\sin\theta_u\sin\phi_u+\zeta(m_r,\mathbf{k},\omega)\cos\theta_u]\} \tag{1}$$

in the molecule-fixed frame of reference. In order to avoid extensive duplication, we have used, unless stated otherwise, in Eq. (1) and throughout this paper much of the notation and assumptions of Refs. 9 and 10 (Ref. 10 will hereafter be referred to as II). The four parameters present in Eq. (1) are[31]

$$\frac{d^2\sigma(m_r)}{d\hat{\mathbf{k}}d\omega}=(-1)^{-1/2}\frac{1}{\sqrt{2\pi}}A_{00}(m_r,\mathbf{k},\omega)\ , \tag{2}$$

$$\chi(m_r,\mathbf{k},\omega)=-\frac{1}{\sqrt{2}}[A_{1,-1}(m_r,\mathbf{k},\omega)-A_{11}(m_r,\mathbf{k},\omega)][A_{00}(m_r,\mathbf{k},\omega)]^{-1}\ , \tag{3}$$

$$\kappa(m_r,\mathbf{k},\omega)=i\frac{1}{\sqrt{2}}[A_{1,-1}(m_r,\mathbf{k},\omega)+A_{11}(m_r,\mathbf{k},\omega)][A_{00}(m_r,\mathbf{k},\omega)]^{-1}\ , \tag{4}$$

and

$$\zeta(m_r,\mathbf{k},\omega)=-A_{10}(m_r,\mathbf{k},\omega)[A_{00}(m_r,\mathbf{k},\omega)]^{-1}\ , \tag{5}$$

where[9,31]

$$\begin{aligned}A_{SM_S}(m_r,\mathbf{k},\omega)=(-1)^{m_r}\sqrt{2S+1}\frac{K}{W_b}\sum_{\mathrm{DS}}\sum_{L,M}\sum_{\substack{\rho,\tau,h,l,m,\nu,\lambda_r\\ \rho',\tau',h',l',m',\nu',\lambda'_r}}&(-i)^{l-l'}\exp[i(\sigma_l-\sigma_{l'})]\\ &\times(-1)^{m+\lambda_r-\nu}\sqrt{(2l+1)(2l'+1)(2L+1)}\\ &\times\begin{bmatrix}\frac{1}{2} & \frac{1}{2} & S\\ -\nu & \nu' & M_S\end{bmatrix}\begin{bmatrix}l & l' & L\\ 0 & 0 & 0\end{bmatrix}\\ &\times\begin{bmatrix}l & l' & L\\ -m & m' & M\end{bmatrix}b^{\rho\tau}_{hlm}b^{\rho'\tau'*}_{h'l'm'}d^{\rho\tau}_{hl\nu,b}(\lambda_r)d^{\rho'\tau'*}_{h'l'\nu',b}(\lambda'_r)Y^M_L(\mathbf{k})\\ &\times\sum_{L_r,M_r}(2L_r+1)\begin{bmatrix}1 & 1 & L_r\\ -m_r & m_r & 0\end{bmatrix}\begin{bmatrix}1 & 1 & L_r\\ -\lambda_r & \lambda'_r & M_r\end{bmatrix}\mathcal{D}^{L_r}_{M_r0}(\omega)\ .\end{aligned} \tag{6}$$

On substituting $A_{00}(m_r,\mathbf{k},\omega)$, obtained by taking $(S,M_S)=(0,0)$ in (6), in the expression (2), one finds that the resulting expression for $d^2\sigma(m_r)/d\hat{\mathbf{k}}\,d\omega$ is equivalent to the angular distribution (11) derived in Ref. 23 for spin-unresolved photoelectrons from oriented molecules. This expression has successfully been used in studying[24,25] the $CF_4(4a_1^2)^{-1}$, $CCl_4(6a_1^2)^{-1}$, and $SiCl_4(7a_1^2)^{-1}$ ARPES and also[29] in predicting and analyzing the circular dichroism in photoelectron angular distribution of nonlinear molecules oriented in space.

It is obvious from the relation (6) that each of the four parameters present in the angular distribution (1) of spin-resolved $E1$ electrons ejected from an oriented, but unpolarized molecule, depends upon the experimental configuration (i.e., the propagation direction $\hat{\mathbf{k}}$ of the photoelectron and orientation ω of the molecule in space), including the state of polarization, in addition to the energy, of the incident radiation. The orders of the harmonics in the polar angles $\hat{\mathbf{k}}(\theta,\phi)$ present in these expressions are $|l-l'|\le L\le l+l'$, with $|M|\le L$.

In contrast to (1), the angular distribution of $E1$ photoelectrons ejected with spin component $\mu_0\hbar$ along $\hat{\mathbf{u}}'(\theta_{u'},\phi_{u'})$ into the solid angle $d\hat{\mathbf{k}}'$ about the direction of propagation $\mathbf{k}'(k,\theta',\phi')$ from a freely rotating molecule is given in Eq. (35a) of I [abbreviated as Eq. (I.35a)].[33] Here, both the propagation vector $\mathbf{k}'$ and the spin-quantization direction $\hat{\mathbf{u}}'$ of the photoelectron are referred to the photon frame of reference. Although, unlike in (1), the number of parameters in the angular distribution (I.35a) is five, they depend only on the energy of the ejected electron. Also, maximum order of the harmonics in $\hat{\mathbf{k}}'(\theta',\phi')$ present in (I.35a) is only 2. Because the differential cross section for ionization in a randomly oriented molecule in the absence of any spin detection of the photoelectrons is[34]

$$\frac{d\bar{\sigma}(m_r)}{d\hat{\mathbf{k}}'}=\frac{\bar{\sigma}}{4\pi}g(m_r;\theta')\ , \tag{7a}$$

with

$$g(m_r;\theta')=1+\tfrac{1}{2}(2-3m_r^2)\bar{\beta}P_2(\cos\theta')\ , \tag{7b}$$

the spin-resolved angular distribution (I.35a) can therefore be written as

$$\frac{d\bar{\sigma}(m_r,\hat{\mathbf{u}}',\mu_0)}{d\hat{\mathbf{k}}'}=\frac{1}{2}\frac{d\bar{\sigma}(m_r)}{d\hat{\mathbf{k}}'}\{1+2\mu_0[\gamma'(m_r,\mathbf{k}')f_1(\hat{\mathbf{u}}')+\bar{\delta}'(m_r,\mathbf{k}')f_2(\hat{\mathbf{u}}')+\xi'(m_r,\mathbf{k}')f_3(\hat{\mathbf{u}}')]\}\ , \tag{8}$$

where appropriate expressions for the coefficients present on the right-hand side of (8) are obtained by comparing it with (I.35a).

Although the structures of the angular distributions (1) and (8) for spin-resolved electrons ejected from oriented and freely rotating molecular targets, respectively, are identical, the important differences between the two are that the four parameters $d^2\sigma/d\hat{\mathbf{k}}\,d\omega$, χ, κ, and ζ present in (1) also depend upon the orientation of the molecule in space and have harmonics in $\hat{\mathbf{k}}$ of maximum order $l+l'$. It is because of these reasons that ASRPES of oriented molecules not only reveals the influence of the fixed molecular orientation on the photoemission process, but also provides an insight into the anisotropic, electron-ion final-state interaction better than what could be gained from ASRPES of molecular systems freely rotating in space. Consequently, as mentioned in the Introduction to this paper, the angular distributions of spin-resolved photoelectrons from molecules oriented in space potentially are a much richer source of information, sensitive probes of photoionization dynamics, and also stringent tests for theoretical models.

The degree of spin polarization along $\hat{\mathbf{u}}$ of electrons ejected with propagation vector $\mathbf{k}$ by interaction of an oriented molecule with light whose state of polarization is specified by m_r is

$$\begin{aligned}P(m_r,\hat{\mathbf{u}},\mathbf{k},\omega)=&\left[\frac{d^2\sigma(m_r,\hat{\mathbf{u}},\nu_0=+\frac{1}{2})}{d\hat{\mathbf{k}}\,d\omega)}-\frac{d^2\sigma(m_r,\hat{\mathbf{u}},\nu_0=-\frac{1}{2})}{d\hat{\mathbf{k}}\,d\omega}\right]\\&\times\left[\frac{d^2\sigma(m_r,\hat{\mathbf{u}},\nu_0=+\frac{1}{2})}{d\hat{\mathbf{k}}\,d\omega}+\frac{d^2\sigma(m_r,\hat{\mathbf{u}},\nu_0=-\frac{1}{2})}{d\hat{\mathbf{k}}\,d\omega}\right]^{-1}\ .\end{aligned} \tag{9}$$

By substituting (1), we find

$$\begin{aligned}P(m_r,\hat{\mathbf{u}},\mathbf{k},\omega)=&\chi(m_r,\mathbf{k},\omega)\sin\theta_u\cos\phi_u\\&+\kappa(m_r,\mathbf{k},\omega)\sin\theta_u\sin\phi_u\\&+\zeta(m_r,\mathbf{k},\omega)\cos\theta_u\ .\end{aligned} \tag{10}$$

Thus the degree of spin polarization of photoelectrons from a molecule with a fixed orientation in space is completely determined by χ, κ, and ζ. These are therefore appropriately called the three spin or polarization parameters. We will see in the following section that these parameters completely vanish in the absence of SOI, yielding no spin selection of photoelectrons.

One of the interesting and simple orientations of a molecule in photoionization experiments is to have its axis parallel to the polar axis of the photon frame.[24] Mathematically, it, in terms of the Euler angles, means[35] $\beta=0$, i.e., $\omega=(\alpha 0\gamma)\equiv\omega_0$ with[35]

$$\mathcal{D}^j_{m'm}(\omega_0)=\exp(im'\gamma)\exp(im\alpha)\delta_{mm'}\ .$$

When using this property of $\mathcal{D}$ functions and orthogonality of 3-j symbols, the expression (6) reduces to the following simple form:

$$
\begin{aligned}
A_{SM_S}(m_r,\mathbf{k},\omega_0) &\equiv A_{SM_S}(m_r,\mathbf{k}) \\
&= \sqrt{2S+1}\,\frac{K}{W_b}\sum_{\mathrm{DS}}\sum_{L,M}\sum_{\substack{\rho,\tau,h,l,m,\nu\\ \rho',\tau',h',l',m',\nu'}} (-i)^{l-l'}\exp[i(\sigma_l-\sigma_{l'})](-1)^{m-\nu} \\
&\quad\times\sqrt{(2l+1)(2l'+1)(2L+1)}\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S \\ -\nu & \nu' & M_S \end{pmatrix} \\
&\quad\times\begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l & l' & L \\ -m & m' & M \end{pmatrix} b^{\rho\tau}_{hlm} b^{\rho'\tau'*}_{h'l'm'} d^{\rho\tau}_{hl\nu;b}(m_r) d^{\rho'\tau'*}_{h'l'\nu';b}(m_r) Y^M_L(\hat{\mathbf{k}}) \;. \qquad (11)
\end{aligned}
$$

It has earlier been mentioned here and elsewhere[9] that the propagation vector $\mathbf{k}(k,\theta,\phi)$ of the ejected electron is referred to the molecule frame. The expression (11) therefore corresponds to the situation when the polar axis of the photon frame, the axis of the oriented molecule, and the photoelectron [for all possible values of the ejection angles (θ,ϕ)] lie in the same plane. It is obvious from our choice of the laboratory- and molecule-fixed frames of reference that in such a coplanar experimental configuration the polar angle θ will always be the same but the azimuthal angle ϕ may differ in the two coordinate systems. Second, in this experimental arrangement, the electric vector for linearly polarized $(m_r=0)$ light will be parallel to the molecular axis. If, on the other hand, the photon beam is circularly polarized or unpolarized [which can be though of as an even mixture of left $(m_r=-1)$ and right $(m_r=+1)$ circularly polarized light], the electric vector will be perpendicular to the axis of the oriented molecule.

III. SPIN-RESOLVED PHOTOIONIZATION IN THE a_1 ORBITAL OF ORIENTED T_d MOLECULES

A. Photoelectron angular distribution

We are interested in this paper in photoionization in the a_1 orbital of a T_d molecule with fixed orientation in space. Group-theoretical considerations show that for an allowed $E1$ transition in the absence of SOI, the continuum orbital of the photoelectron should transform according to the triply degenerate T_2 irreducible representation (IR) of this point group.[36] Consequently, we have in the formulas given in the preceding section $p=p'=t_2$ with $\tau=1-3$ for $a_1\rightarrow kt_2$ allowed $E1$ transition in a T_d molecule. There is only one basis function (generalized harmonics) up to the gth (i.e., $l=4$) partial wave which may be used to represent the ejected electron.[23] Hence $h=h'=1$ for each of the values of $l,l'\leq 4$ included in the various expressions given in Sec. II. On invoking the two assumptions already discussed in Ref. 10 [namely, (i) the initial bound state for M and the final state for the $e+M^+$ system are each represented by a single Slater determinant consisting of only one-electron orbitals expanded about the center of mass of the target in the molecule frame of reference; (ii) neglect the core-relaxation effects], the photoionization matrix elements $d^{\rho\tau}_{hl\nu,b}(\lambda_r)$ reduce to the one-electron dipole integral given in Eq. (II.1). These assumptions also mean[10] that $W_b=2$ and $\sum_{\mathrm{DS}}\equiv\sum_{\nu_b=-1/2}^{+1/2}$ in the preceding section. Here $\nu_b\hbar$, with $\nu_b=\pm\frac{1}{2}$, is the component along the molecular axis of the bound electron's spin angular momentum.

Let us consider, for simplicity, the desired $a_1\rightarrow kt_2$ (bound-free) transition in an oriented T_d molecule in a coplanar experimental configuration. In view of the discussion given in the preceding paragraph, one readily obtains the following expressions from Eq. (11):

$$
\begin{aligned}
A_{00}(m_r,\mathbf{k}) &= (-1)^{1/2}\frac{K}{2\sqrt{2}} \\
&\quad\times\sum_{\nu_b=-1/2}^{1/2}\;\sum_{L=|l-l'|}^{l+l'}\;\sum_{M=-L}^{L}\;\sum_{\tau,\tau'=1}^{3}\;\sum_{\substack{l,m\\ l',m'}} (-i)^{l-l'}e^{i(\sigma_l-\sigma_{l'})}(-1)^m\sqrt{(2l+1)(2l'+1)(2L+1)}\begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \\
&\quad\times\begin{pmatrix} l & l' & L \\ -m & m' & M \end{pmatrix} b^{\tau}_{lm} b^{\tau'*}_{l'm'} Y^M_L(\hat{\mathbf{k}})\sum_{\nu} d^{\tau}_{l\nu,\nu_b}(m_r) d^{\tau'*}_{l'\nu',\nu_b}(m_r) \;, \qquad (12)
\end{aligned}
$$

$$A_{1,-1}(m_r,\mathbf{k})\pm A_{11}(m_r,\mathbf{k})$$
$$=(-1)^{\pm 1/2}\frac{K}{2}\sum_{\nu_b=-1/2}^{1/2}\ \sum_{L=|l-l'|}^{L}\ \sum_{M=-L}^{L}\ \sum_{\tau,\tau'=1}^{3}\ \sum_{\substack{l,m\\ l',m'}}(-i)^{l-l'}\exp[i(\sigma_l-\sigma_{l'})](-1)^m$$
$$\times\sqrt{(2l+1)(2l'+1)(2L+1)}\begin{bmatrix} l & l' & L\\ 0 & 0 & 0\end{bmatrix}$$
$$\times\begin{bmatrix} l & l' & L\\ -m & m' & M\end{bmatrix} b_{lm}^{\tau} b_{l'm'}^{\tau'^*} Y_L^M(\hat{\mathbf{k}})[d_{l,1/2,\nu_b}^{\tau}(m_r)d_{l',-1/2,\nu_b}^{\tau'^*}(m_r)$$
$$\mp d_{l,-1/2,\nu_b}^{\tau}(m_r)d_{l'1/2,\nu_b}^{\tau'^*}(m_r)]\ , \tag{13}$$

and

$$A_{10}(m_r,\mathbf{k})=\frac{K}{2\sqrt{2}}\sum_{\nu_b=-1/2}^{1/2}\ \sum_{L=|l-l'|}^{l+l'}\ \sum_{M=-L}^{L}\ \sum_{\tau,\tau'=1}^{3}\ \sum_{\substack{l,m\\ l',m'}}(-i)^{l-l'}\exp[i(\sigma_l-\sigma_{l'})](-l)^m\sqrt{(2l+1)(2l'+1)(2L+1)}\begin{bmatrix} l & l' & L\\ 0 & 0 & 0\end{bmatrix}$$
$$\times\begin{bmatrix} l & l' & L\\ -m & m' & M\end{bmatrix} b_{lm}^{\tau} b_{l'm'}^{\tau'^*} Y_L^M(\hat{\mathbf{k}})\sum_{\nu}(-1)^{-\nu}d_{l\nu,\nu_b}^{\tau}(m_r)d_{l'\nu,\nu_b}^{\tau'^*}(m_r)\ . \tag{14}$$

In Eqs. (12)–(14) and hereafter, all subscripts and/or superscripts whose absence does not obscure the meaning of an expression have not been written, for brevity.

In order to proceed further one needs to know the one-electron dipole integrals $d_{l\nu,\nu_b}^{\tau}(m_r)$ present in (12)–(14). The evaluation of these ionization amplitudes has already been discussed at length in II. The essential points of that discussion, relevant to our present study, are (i) the spin polarization of photoelectrons ejected in the $a_1^2\rightarrow a_1^1kt_2$ $E1$ transition in a T_d molecule without oriented spins is due only to the SOI in the continuum part of the molecular spectrum; (ii) in order to take the SOI properly into account, one needs to consider the extended[32] T_d point group; (iii) consequently, an electron photoionized from the a_1 bound orbital has available to it two continuum channels belonging to the $E_{5/2}$ and $G_{3/2}$ double-valued[32] IR's of the extended group of T_d molecules; (iv) the corresponding bound-free transitions are therefore $a_1^2\rightarrow a_1^1(e_{1/2})kt_2(e_{5/2})$ and $a_1^2\rightarrow a_1^1(e_{1/2})kt_2(g_{3/2})$, respectively, where both $E_{1/2}$ and $E_{5/2}$ are doubly degenerate and $G_{3/2}$ is a quadruply degenerate IR; (v) the 12 one-electron $E1$ dipole integrals (II.22), corresponding to $\tau=1-3$ and $\nu,\nu_b=\pm\frac{1}{2}$ for each lth partial wave, are obtained using the symmetry adapted basis functions developed by Cracknell and Joshua[37] for these double-valued IR's of the extended T_d point group.

Let us consider two special cases for photoionization in a coplanar experimental arrangement: The electric vector in the incident beam of radiation is oriented (i) parallel and (ii) perpendicular to the molecular axis. These correspond to taking, respectively, $m_r=0$ and $m_r=\pm 1$ in the expressions (12)–(14). On using the ionization amplitudes (II.22) and substituting the appropriate coefficients b_{lm}^{τ} from Appendix 3 in Ref. 23, one specializes (12)–(14) for linearly polarized light if $m_r=0$. In order to see what happens to the consequent expressions for $A_{00}(m_r=0,\mathbf{k})$, $A_{1,-1}(m_r=0,\mathbf{k})\mp A_{11}(m_r=0,\mathbf{k})$, and $A_{10}(m_r=0,\mathbf{k})$ in the absence of SOI in the t_2 orbital of the photoelectron, one merely needs to use therein the relations (II.26). On substituting the resulting four expressions in (2)–(5), respectively, one readily finds that, for photoionization in a coplanar experimental configuration in a molecule oriented with its axis parallel to the electric vector of the linearly polarized light, $d^2\sigma(m_r=0)/d\hat{\mathbf{k}}\,d\omega_0$ is identical to the spin-unresolved photoelectron angular distribution derived by us earlier in Eqs. (5) and (11) in Ref. 24(b); whereas $\chi(m_r=0,\mathbf{k},\omega_0)=\kappa(m_r=0,\mathbf{k},\omega_0)=\zeta(m_r=0,\mathbf{k},\omega_0)=0$. Because the degree of spin-polarization (10) completely depends upon χ, κ, and ζ, the simultaneous vanishing of these three parameters simply means that the electrons ejected in ionization with the electric vector parallel to the molecular axis have no spin selection if the SOI in the $a_1^2\rightarrow a_1^1kt_2$ bound-free transition in an oriented T_d molecule is not taken into account.

In order to know the four parameters $d^2\sigma/d\hat{\mathbf{k}}\,d\omega_0$, χ, κ, and ζ for photoionization with the electric vector perpendicular to the molecular axis in a coplanar experimental arrangement, we need to evaluate the expressions (12)–(14) for $m_r=\mp 1$. Again, on using the dipole moments (II.22), the coefficient b's,[23] and taking $m_r=\mp 1$, one obtains $A_{00}(m_r=\mp 1,\mathbf{k})$, $A_{1,-1}(m_r=\mp 1,\mathbf{k})\mp A_{11}(m_r=\mp 1,\mathbf{k})$, and $A_{10}(m_r=\mp 1,\mathbf{k})$. Employing Eqs. (II.26) and substituting the resulting expressions in the definition (2)–(5), we find that in the absence of SOI, these coefficients give

$$d^2\sigma(m_r=-1)/d\hat{\mathbf{k}}\,d\omega_0\ ,d^2\sigma(m_r=+1)/d\hat{\mathbf{k}}\,d\omega_0\ ,$$

and

$$\chi(m_r=-1,\mathbf{k},\omega_0)=\kappa(m_r=-1,\mathbf{k},\omega_0)$$
$$=\zeta(m_r=-1,\mathbf{k},\omega_0)=\chi(m_r=+1,\mathbf{k},\omega_0)=\kappa(m_r=+1,\mathbf{k},\omega_0)=\zeta(m_r=+1,\mathbf{k},\omega_0)=0\ .$$

The angular distributions $d^2\sigma(m_r=-1)/d\hat{\mathbf{k}}\,d\omega_0$ and $d^2\sigma(m_r=+1)/d\hat{\mathbf{k}}\,d\omega_0$ are exactly the same as given in Eqs. (5) and (16) in Ref. 24(b) in the absence of spin effects. The vanishing of the polarization parameters leads to the conclusion, on combining with the relation (10), that the photoelectrons ejected by left or right circularly polarized light will completely be spin unresolved when the SOI in the continuum orbital in the $a_1^2 \rightarrow a_1^2 kt_2$ transition in a T_d molecule oriented in a coplanar experimental configuration is not included.

All of the coefficient A's thus obtained by taking $m_r=0$ and ± 1 in Eqs. (12)–(14) are exact. The only approximation made in their derivation is that we have considered $l,l'=1$ and 2 in (12)–(14), i.e., represented the photoelectron in its t_2 continuum orbital by p- and d-partial waves. Extension to still higher values of l,l' is straightforward. In the following subsection, these 12 [$A_{00}(m_r=0,\mathbf{k})$, $A_{1,-1}(m_r=0,\mathbf{k})\mp A_{11}(m_r=0,\mathbf{k})$, $A_{10}(m_r=0,\mathbf{k})$, $A_{00}(m_r=\mp 1,\mathbf{k})$, $A_{1,-1}(m_r=\mp 1,\mathbf{k})$ $\mp A_{11}(m_r=\mp 1,\mathbf{k})$, and $A_{10}(m_r=\mp 1,\mathbf{k})$] expressions are used to develop a set of formulas for the analysis of measurements and calculations of the ASRPES of the a_1 orbital in a T_d molecule with a fixed orientation in space.

B. Degree of spin polarization

In order to proceed further, both the magnitude as well as the phase of the $E1$ ionization integrals $R_l(i,q)$, which are defined in Eqs. (II.19) and are present in this paper in the above-mentioned expressions for the coefficient A's through the quantities $R_l(i\pm)$ specified by Eqs. (II.21), are needed. It can be the goal of a particular calculational study to obtain these quantities from *ab initio* methods. In the present work, however, we do not do any dynamical calculations. In order to extract these ionization integrals from whatever experimental information we have on photoionization in the a_1 orbital of a T_d molecule, we follow the same procedure used in II.

Hitherto, the only measurements available to us on photoionization of T_d molecules are of $\bar{\sigma}$ and $\bar{\beta}$ present in the angular distribution (7) for spin-unresolved electrons ejected from a freely rotating target. It is therefore obvious that, in order to be able to use this experimental information, the number of ionization integrals must be reduced. If one considers only the lowest[23] $l_b=0$ term in the single-center expansion (II.2) for the $e_{1/2}$ bound spin-orbital in the target, one then finds from Eqs. (II.42), (II.48a), and (II.48b) that

$$R_l(1;q)=R_l(2;q)\equiv R_l(q) \tag{15a}$$

and

$$R_l(1-)=R_l(2-)=R_l(g_{3/2})-R_l(e_{5/2})\equiv R_l(-)\ ,$$
$$R_l(1+)=R_l(2+)=2R_l(g_{3/2})+R_l(e_{5/2})\equiv R_l(+)\ , \tag{15b}$$

respectively. On using (15b) in the 12 expressions for A's, we find that the number of parameters required in the resulting equations reduces to ten, namely, four moduli $|R_1(+)|^2$, $|R_1(-)|^2$, $|R_2(+)|^2$, and $|R_2(-)|^2$ associated with p and d waves of the photoelectron, plus six phases, one each for the products $R_1(+)R_1^*(-)$, $R_2(+)R_2^*(-)$, $R_1(+)R_2^*(+)$, $R_1(+)R_2^*(-)$, $R_1(-)R_2^*(+)$, and $R_1(-)R_2^*(-)$.

Following II, we introduce here one more approximation by representing the photoelectron by a single $p(l=1)$ partial wave. One cannot obviously expect that such simple considerations will adequately describe the angle- and spin-resolved photoionization in the a_1 orbital of a T_d molecule with a fixed orientation in space. However, the motivation for the present study is, among other things, to show how the multichannel theory developed in Ref. 9 for ASRPES studies in molecules with a fixed orientation in space can be applied to a real situation, how the use of the group-theoretical methods simplifies an otherwise extremely complex problem to maximum possible extent making the solution very transparent and readily interpretable, and to demonstrate that, similar to the case of freely rotating molecules, spin-resolved electrons can in general be obtained from photoionization of even oriented, but unpolarized, nonlinear targets by linearly, circularly polarized, or unpolarized light when only the SOI is present, and that, too, merely in the continuum part of the molecular spectrum. Therefore, while the procedure followed and the formulas derived in this paper develop a methodology and set a framework for the analysis of measurements and calculations of spin-resolved spectra in these oriented molecules, our results serve as a reference point for comparing more involved calculations that properly take into account the anisotropic interaction between the photoelectron and the residual molecule, in addition to representing the bound and continuum orbitals more satisfactorily. Needless to say, it will be prohibitively difficult to perform such *ab initio* calculations for complicated nonlinear molecules whose point symmetry group is T_d and have a fixed orientation in space.

Furthermore, because the present work is based on almost identical approximations used in II, it therefore facilitates a direct comparison between the ASRPES studies of molecular targets with and without a fixed orientation in space. Such studies will be helpful in understanding how much additional information on photoionization dynamics can be obtained and physical insight gained by studying angular distribution of spin-resolved photoelectrons ejected from oriented molecules compared to the knowledge achieved from similar studies in freely rotating targets. One will thus be able to understand better the influence of molecular orientation on spin-resolved photoelectron emission processes in molecules.

On introducing the above-mentioned approximation in $A_{00}(m_r=0,\mathbf{k})$, $A_{1,-1}(m_r=0,\mathbf{k})\mp A_{11}(m_r=0,\mathbf{k})$, and $A_{10}(m_r=0,\mathbf{k})$ and substituting the resulting expressions in (2)–(5), respectively, we find that the following parameters:

$$\frac{d^2\sigma^{\parallel}}{d\hat{\mathbf{k}}\,d\omega_0}\equiv\frac{d^2\sigma(m_r=0)}{d\hat{\mathbf{k}}\,d\omega_0}=\frac{K}{12\pi}(\sin^2\theta+|X_1|^2\cos^2\theta)|R_1^{(-)}|^2\ , \tag{16}$$

$$\chi^{\parallel}(\mathbf{k})\equiv\chi(m_r=0,\mathbf{k},\omega_0)=2\frac{|X_1|\cos\Delta_1}{|X_1|^2+\tan^2\theta}\tan\theta\sin\phi\ , \tag{17a}$$

$$\kappa^{\parallel}(\mathbf{k})\equiv\kappa(m_r=0,\mathbf{k},\omega_0)=-2\frac{|X_1|\sin\Delta_1}{|X_1|^2+\tan^2\theta}\tan\theta\cos\phi\ , \tag{17b}$$

and

$$\zeta^{\parallel}(\mathbf{k})\equiv\zeta(m_r=0,\mathbf{k},\omega_0)=-\frac{\tan^2\theta\sin2\phi}{|X_1|^2+\tan^2\theta}\ , \tag{17c}$$

completely characterize the angular distribution

$$\frac{d^2\sigma^{\parallel}(\hat{\mathbf{u}},\nu_0)}{d\hat{\mathbf{k}}\,d\omega_0}\equiv\frac{d^2\sigma(m_r=0,\hat{\mathbf{u}},\nu_0)}{d\hat{\mathbf{k}}\,d\omega_0}=\frac{1}{2}\frac{d^2\sigma^{\parallel}}{d\hat{\mathbf{k}}\,d\omega_0}\{1+2\nu_0[\chi^{\parallel}(\mathbf{k})\sin\theta_u\cos\phi_u+\kappa^{\parallel}(\mathbf{k})\sin\theta_u\sin\phi_u+\zeta^{\parallel}(\mathbf{k})\cos\theta_u]\} \tag{18}$$

and the degree of spin polarization

$$P^{\parallel}(\hat{\mathbf{u}},\mathbf{k})\equiv P(m_r=0,\hat{\mathbf{u}},\mathbf{k},\omega_0)=\chi^{\parallel}(\mathbf{k})\sin\theta_u\cos\phi_u+\kappa^{\parallel}(\mathbf{k})\sin\theta_u\sin\phi_u+\zeta^{\parallel}(\mathbf{k})\cos\theta_u \tag{19}$$

of electrons ejected from the a_1 orbital in a T_d molecule oriented with its axis parallel to the electric vector in the plane polarized light. In Eqs. (16) and (17), the complex quantity

$$X_1=R_1(+)/R_1(-)=\frac{2R_1(g_{3/2})+R_1(e_{5/2})}{R_1(g_{3/2})-R_1(e_{5/2})}\ , \tag{20a}$$

$$=|X_1|e^{i\Delta_1}\ , \tag{20b}$$

where $R_1(+)$ and $R_1(-)$ are specified by Eqs. (15).

If one uses (15b) in $A_{00}(m_r=-1,\mathbf{k})$, $A_{1,-1}(m_r=-1,\mathbf{k})\mp A_{11}(m_r=-1,\mathbf{k})$, and $A_{10}(m_r=-1,\mathbf{k})$, represents the photoelectron by a p wave, and then substitutes the resulting four expressions in (2)–(5), respectively, one finds, with the help of the relations (20), that

$$\frac{d^2\sigma(m_r=-1)}{d\hat{\mathbf{k}}\,d\omega_0}=\frac{K}{24\pi}(1+\cos^2\theta+|X_1|^2\sin^2\theta)|R_1(-)|^2\ , \tag{21a}$$

$$\chi(m_r=-1,\mathbf{k},\omega_0)=\frac{|X_1|\sin(\phi-\Delta_1)-\sin\phi}{1+|X_1|^2\sin^2\theta+\cos^2\theta}\sin2\theta\ , \tag{21b}$$

$$\kappa(m_r=-1,\mathbf{k},\omega_0)=-\frac{|X_1|\sin|(\phi-\Delta_1)+\sin\phi}{1+|X_1|^2\sin^2\theta+\cos^2\theta}\sin2\theta\ , \tag{21c}$$

and

$$\zeta(m_r=-1,\mathbf{k},\omega_0)=2\frac{|X_1|\sin(2\phi-\Delta_1)}{1+|X_1|^2\sin^2\theta+\cos^2\theta}\sin^2\theta\ , \tag{21d}$$

for photoionization in a coplanar experimental setup in the a_1 orbital of a T_d molecule by left circularly polarized light.

The four corresponding parameters

$$\frac{d^2\sigma(m_r=+1)}{d\hat{\mathbf{K}}\,d\omega_0}=\frac{K}{24\pi}(1+|X_1|^2\sin^2\theta+\cos^2\theta)\times|R_1(-)|^2\ , \tag{22a}$$

$$\chi(m_r=+1,\mathbf{k},\omega_0)=\frac{|X_1|\sin(\phi+\Delta_1)-\sin\phi}{1+|X_1|^2\sin^2\theta+\cos^2\theta}\sin2\theta\ , \tag{22b}$$

$$\kappa(m_r=+1,\mathbf{k},\omega_0)=\frac{|X_1|\sin(\phi+\Delta_1)+\sin\phi}{1+|X_1|^2\sin^2\theta+\cos^2\theta}\sin2\theta\ , \tag{22c}$$

and

$$\zeta(m_r=+1,\mathbf{k},\omega_0)=2\frac{|X_1|\sin(2\phi+\Delta_1)}{1+|X_1|^2\sin^2\theta+\cos^2\theta}\sin^2\theta\ , \tag{22d}$$

for photoionization by right circularly polarized light are obtained by substituting the respective relations $A_{00}(m_r=+1,k)$, $A_{1,-1}(m_r=+1,k)\mp A_{11}(m_r=+1,k)$, and $A_{10}(m_r=+1,k)$ in (2)–(5), using the above discussed approximations, and the definition (20).

The photoelectron angular distribution for ionization with the electric vector perpendicular to the axis of a molecule oriented in a coplanar experimental arrangement is given by[24(b)]

$$\frac{d^2\sigma^{\perp}(\hat{\mathbf{u}},\nu_0)}{d\hat{\mathbf{k}}\,d\omega_0}=\frac{1}{2}\left[\frac{d^2\sigma(m_r=-1,\hat{\mathbf{u}},\nu_0)}{d\hat{\mathbf{k}}\,d\omega_0}+\frac{d^2\sigma(m_r=+1,\hat{\mathbf{u}},\nu_0)}{d\hat{\mathbf{k}}\,d\omega_0}\right]. \tag{23}$$

We already know from (21a) and (22a) that

$$\frac{d^2\sigma(m_r=-1)}{d\hat{\mathbf{k}}\,d\omega_0}=\frac{d^2\sigma(m_r=-1)}{d\hat{\mathbf{k}}\,d\omega_0}\equiv\frac{d^2\sigma^{\perp}}{d\hat{\mathbf{k}}\,d\omega_0}=\frac{K}{24\pi}(1+|X_1|^2\sin^2\theta+\cos^2\theta)|R_1(-)|^2 \tag{24}$$

and if we define

$$\chi^{\perp}(\mathbf{k})=\tfrac{1}{2}[\chi(m_r=-1,\mathbf{k},\omega_0)+\chi(m_r=+1,\mathbf{k},\omega_0)]\ , \tag{25}$$

with similar expressions for $\kappa^{\perp}(\mathbf{k})$ and $\zeta^{\perp}(\mathbf{k})$, the spin-resolved photoelectron angular distribution (23) can be written as

$$\frac{d^2\sigma^{\perp}(\hat{\mathbf{u}},\nu_0)}{d\hat{\mathbf{k}}\,d\omega_0}=\frac{1}{2}\frac{d^2\sigma^{\perp}}{d\hat{\mathbf{k}}\,d\omega_0}\{1+2\nu_0[\chi^{\perp}(\mathbf{k})\sin\theta_u\cos\phi_u+\kappa^{\perp}(\mathbf{k})\sin\theta_u\sin\phi_u+\zeta^{\perp}(\mathbf{k})\cos\theta_u]\}\;. \tag{26}$$

Equations (10) and (25) give the degree of spin polarization

$$P^{\perp}(\hat{\mathbf{u}},\mathbf{k})=\chi^{\perp}(\mathbf{k})\sin\theta_u\cos\phi_u+\kappa^{\perp}(\mathbf{k})\sin\theta_u\sin\phi_u+\zeta^{\perp}(\mathbf{k})\cos\theta_u \tag{27}$$

along $\hat{\mathbf{u}}$ of electrons ejected in a coplanar experimental arrangement from the a_1 orbital in a T_d molecule oriented with its axis perpendicular to the electric vector of the incident beam of photons.

On substituting the relations (21) and (22) in the definitions (25), we find that the explicit expressions for the three parameters needed in both (26) and (27) are

$$\chi^{\perp}(\mathbf{k})=\frac{|X_1|\cos\Delta_1-1}{1+|X_1|^2\sin^2\theta+\cos^2\theta}\sin2\theta\sin\phi\;, \tag{28a}$$

$$\kappa^{\perp}(\mathbf{k})=\frac{|X_1|\sin\Delta_1}{1+|X_1|^2\sin^2\theta+\cos^2\theta}\sin2\theta\cos\phi\;, \tag{28b}$$

and

$$\zeta^{\perp}(\mathbf{k})=2\frac{|X_1|\cos\Delta_1}{1+|X_1|^2\sin^2\theta+\cos^2\theta}\sin^2\theta\sin2\phi\;. \tag{28c}$$

C. Properties of the polarization parameters

Each of the three expressions (17a)–(17c) and (28a)–(28c) for the polarization parameters $(\chi^{\parallel},\kappa^{\parallel},\zeta^{\parallel})$ and $(\chi^{\perp},\kappa^{\perp},\zeta^{\perp})$, respectively, can readily be shown to have the following properties with respect to the phase $\Delta_1(=0-2\pi)$, and the spherical angles $\theta(=0-\pi)$, $\phi(=0-2\pi)$ of the propagation direction **k**

Property 1. We have

$$\chi^{\parallel}(\mathbf{k})=0=\zeta^{\perp}(\mathbf{k})\quad\text{for } \Delta_1=\pi/2,3\pi/2\;, \tag{29a}$$

$$\kappa^{\parallel}(\mathbf{k})=0=\kappa^{\perp}(\mathbf{k})\quad\text{for } \Delta_1=n\pi, n=0-2\;, \tag{29b}$$

$$\chi^{\perp}(\mathbf{k})=0\quad\text{for } \Delta_1=\cos^{-1}(|X_1|^{-1})\;, \tag{29c}$$

Property 2. We have

$$\chi^{\parallel}(\mathbf{k})=\kappa^{\parallel}(\mathbf{k})=\zeta^{\parallel}(\mathbf{k})=\chi^{\perp}(\mathbf{k})=\kappa^{\perp}(\mathbf{k})=\zeta^{\perp}(\mathbf{k})=0\;, \tag{30}$$

for $\theta=0$ and π. Consequently, from Eqs. (19) and (27), respectively,

$$P^{\parallel}(\hat{\mathbf{u}},\mathbf{k})=0=P^{\perp}(\hat{\mathbf{u}},\mathbf{k})\;, \tag{31a}$$

for these values of θ. Hence the photoelectrons are completely spin unpolarized if moving out from the a_1 orbital in a T_d molecule along its axis oriented in space either parallel or perpendicular to the electric vector of the ionizing radiation. Further, from Eqs. (17) and (28)

$$\chi^{\parallel}(\mathbf{k})=\kappa^{\parallel}(\mathbf{k})=\chi^{\perp}(\mathbf{k})=\kappa^{\perp}(\mathbf{k})=0\;, \tag{30$'$}$$

$$\zeta^{\parallel}(\mathbf{k})=-\sin2\phi\;, \tag{30$''$}$$

$$\zeta^{\perp}(\mathbf{k})=2|X_1|\frac{\cos\Delta_1\sin2\phi}{1+|X_1|^2}\;, \tag{30$'''$}$$

for photoelectrons moving perpendicular to the molecular axis. Thus, while $\zeta^{\perp}$ still depends both on the magnitude $|X_1|$ and the phase Δ_1 of X_1, $\zeta^{\parallel}$ becomes completely independent of the energy of the ionizing radiation and is simply proportional to the sine of twice the azimuthal angle specifying the direction of propagation $\hat{\mathbf{k}}(\pi/2,\phi)$ of the photoelectron. The degrees (19) and (27) of spin polarization respectively become

$$P^{\parallel}(\hat{\mathbf{u}},\mathbf{k})=-\sin2\phi\cos\theta_u \tag{31b}$$

and

$$P^{\perp}(\hat{\mathbf{u}},\mathbf{k})=2|X_1|\frac{\cos\Delta_1\sin2\phi}{1+|X_1|^2}\cos\theta_u \tag{31c}$$

for $\theta=\pi/2$.

Property 3. We have

$$\chi^{\parallel}(\mathbf{k})=\zeta^{\parallel}(\mathbf{k})=\chi^{\perp}(\mathbf{k})=\zeta^{\perp}(\mathbf{k})=0 \tag{32a}$$

for $\phi=n\pi$ with $n=0-2$, i.e., **k** in the x-z plane; and

$$\kappa^{\parallel}(\mathbf{k})=\zeta^{\parallel}(\mathbf{k})=\kappa^{\perp}(\mathbf{k})=\zeta^{\perp}(\mathbf{k})=0 \tag{32b}$$

for $\phi=\pi/2$ and $3\pi/2$, i.e., **k** in the y-z plane.

D. Results

In order to be able to calculate the polarization parameters $(\chi^{\parallel},\kappa^{\parallel},\zeta^{\parallel})$ and $(\chi^{\perp},\kappa^{\perp},\zeta^{\perp})$ from Eqs. (17) and (28), respectively, one needs to know both the magnitude $|X_1|$ and the phase Δ_1 of X_1. These quantities are defined in Eqs. (20) and can be obtained from a knowledge of any two of the six observables given in the two sets of Eqs. (17) and (28). Measurements of $\zeta^{\parallel}(\mathbf{k})$ will directly give us the magnitude $|X_1|$ from Eq. (17c). The phase Δ_1 can, on the other hand, be determined from any of the five relations (17a), (17b), and (28a)–(28c). Out of these, only two [i.e., (17b) and (28b)] depend on the sine of Δ_1; whereas the rest involve the cosine of Δ_1. Hence a measurement of $\kappa^{\parallel}$ or of $\kappa^{\perp}$ will give us information on both sign and magnitude of Δ_1.

The three examples considered in this paper are photoionization in $4a_1^2$, $6a_1^2$, and $7a_1^2$ orbitals of oriented CF_4, CCl_4, and $SiCl_4$, respectively. The only measurements available to us in all these cases are of the integrated partial cross section $\bar{\sigma}$ and of the asymmetry $\bar{\beta}$ present in the angular distribution (7) for spin-unresolved photoelectrons, ejected from freely rotating targets. We have already shown in II that $|X_1|$ and $\bar{\beta}$ under the similar approximations used herein are related to each other by

$$|X_1|^2 = 2\frac{1/5+\bar{\beta}}{2-\bar{\beta}} \qquad (33)$$

for spin-resolved photoionization in the a_1 orbital of a randomly oriented T_d molecule.

It is well known that the asymmetry in the angular distribution of photoelectrons ejected in ionization of unoriented molecules is always $-1 \le \bar{\beta} \le 2$. Equation (33) will therefore give $|X_1|^2$ to be negative if $-1 \le \bar{\beta} < -\frac{1}{5}$. For all the T_d molecules,[38-43] whose ARPES of the a_1 orbital has so far been taken, $\bar{\beta}$ is always greater than $-\frac{1}{5}$. Equation (33) can therefore be used to extract the magnitude of X_1 from the experimental measurements of $\bar{\beta}$ in all such cases. Equations (17c), which do not involve the phase Δ_1, should therefore describe the energy-dependent behavior of $\zeta^{\parallel}$. The applications of the rest of the equations mentioned earlier require, on the other hand, a knowledge of the phase Δ_1 which has here been treated as a parameter. The results presented in the following subsections are based on Eqs. (17) and (28).

We found that if one knows $\chi^{\parallel}$ and $\kappa^{\parallel}$ for $(0 \le \Delta_1, \theta, \phi \le \pi/2)$, $\zeta^{\parallel}$ for $(0 \le \theta \le \pi/2, 0 \le \phi \le \pi/4)$, $\chi^{\perp}$ for $(0 \le \Delta_1 \le \pi, 0 \le \theta \le \pi/4, 0 \le \phi \le \pi/2)$, $\kappa^{\perp}$ for $(0 \le \Delta_1 \le \pi/2, 0 \le \theta \le \pi/4, 0 \le \phi \le \pi/2)$, and $\zeta^{\perp}$ for $(0 \le \Delta_1 \le \pi/2, 0 \le \theta \le \pi/2, 0 \le \phi \le \pi/4)$, the values of the six polarization parameters outside these ranges for Δ_1, θ, and ϕ can readily be obtained by using the various properties of the trigonometric functions present in the expressions (17a)–(17c), (28a)–(28c), respectively.

1. Photoionization in the $4a_1^2$ orbital of CF$_4$

Carlson *et al.*[40] have extracted both $\bar{\sigma}$ and $\bar{\beta}$ from their ARPES of the $4a_1^2$ orbital in gaseous, unoriented CF$_4$ for incident photon energies from 28 to 70 eV. Novak *et al.*[41] have also reported measurements of $\bar{\beta}$ for this process. There is, in general, good agreement on the angular asymmetry measured by the two different groups. Because $\bar{\beta}$ in this case is always greater than $-\frac{1}{5}$, it can therefore be used in Eq. (33) to extract $|X_1|$.

Figure 1(a) contains the polarization parameter $\chi^{\parallel}(\mathbf{k})$ calculated from Eq. (17a) for ionization with the electric vector parallel to the molecular axis. The shape of the curves for all values of Δ_1, θ, ϕ considered in Fig. 1(a) are almost the same; in all cases $\chi^{\parallel}$ has a valley between 30 and 35 eV photon energy. However, the magnitude of $\chi^{\parallel}$ with $\Delta_1 = 0$ is much larger, and so are the minima much deeper, than for $\Delta_1 = \pi/4$.

The spin parameter $\kappa^{\parallel}(\mathbf{k})$ calculated from Eq. (17b) is shown in Fig. 1(b). The behavior of $\kappa^{\parallel}$ as a function of photon energy is almost a mirror image of that shown in Fig. 1(a) for $\chi^{\parallel}$. $\kappa^{\parallel}$ is thus negative for the values of Δ_1, θ, ϕ considered in Fig. 1(b) and the valley in 1(a) is reversed into a peak here.

The third parameter $\zeta^{\parallel}$, needed to describe the degree (19) of spin polarization of photoelectrons ejected from the $4a_1^2$ orbital of CF$_4$ oriented with its axis parallel to the electric vector of linearly polarized incident light, is shown in Fig. 1(c). This result is independent of the phase Δ_1 and has been calculated from the expression

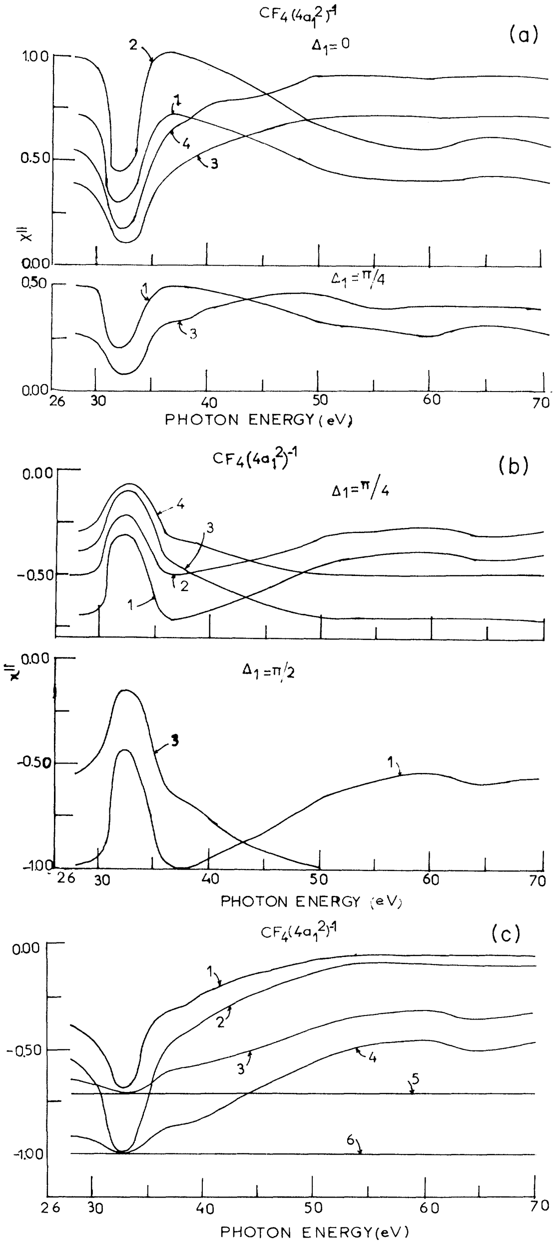

FIG. 1. (a) Variation of $\chi^{\parallel}(\mathbf{k})$ with photon energy for ionization in the $4a_1^2$ orbital of CF$_4$ oriented with its axis parallel to the electric vector in the linearly polarized incident light. The $|X_1|$ used in the expression (17a) was obtained by substituting $\bar{\beta}$, measured by Carlson *et al.* (Ref. 40) in Eq. (33). The values of $(\theta,\phi) = (\pi/6, \pi/4)$ for curve 1, $(\pi/6, \pi/2)$ for curve 2, $(\pi/3, \pi/4)$ for curve 3, $(\pi/3, \pi/2)$ for curve 4. In view of the expression (17a), curve 2 and curve 4 for $\Delta_1 = \pi/4$ are exactly the same as the respective curve 1 and curve 3 with $\Delta_1 = 0$. (b) Same as (a) but for $\kappa^{\parallel}(\mathbf{k})$ calculated from the expression (17b). $(\theta,\phi) = (\pi/6, 0)$ for curve 1, $(\pi/6, \pi/4)$ for curve 2, $(\pi/3, 0)$ for curve 3, $(\pi/3, \pi/4)$ for curve 4. Curve 2 and curve 4 for $\Delta_1 = \pi/2$ are exactly the same as curve 1 and curve 3 with $\Delta_1 = \pi/4$, respectively. (c) Same as (a) but for $\zeta^{\parallel}(\mathbf{k})$ calculated from the expression (17c). This parameter is independent of the phase Δ_1, and the values of $(\theta,\phi) = (\pi/6, \pi/8)$ for curve 1, $(\pi/6, \pi/4)$ for curve 2, $(\pi/3, \pi/8)$ for curve 3, $(\pi/3, \pi/4)$ for curve 4, $(\pi/2, \pi/8)$ for curve 5, $(\pi/2, \pi/4)$ for curve 6.

(17c). Although $\zeta^{\parallel}$ is negative for the values of (θ,ϕ) considered in Fig. 1(c), its behavior as a function of energy of the ionizing radiation is almost the same as that of $\chi^{\parallel}$ shown in Fig. 1(a). Furthermore, unlike the two other parameters, $\zeta^{\parallel}$ does not vanish for $\theta=\pi/2$; it instead becomes equal to $-\sin 2\phi$ as shown in Eq. (30″). Therefore, when the photoelectron is moving perpendicularly to the molecular axis, $\zeta^{\parallel}$ is independent of its energy. Moreover, $\zeta^{\parallel}$ obviously becomes zero if the photoelectron goes out in the X-Z or Y-Z planes.

The three polarization parameters for photoionization in the $4a_1^2$ orbital of CF_4 with the electric vector perpendicular to the molecular axis are shown in Figs. 2(a)–2(c). The first of the three figures contains $\chi^{\perp}$ calculated from (28a). Here we find that $\chi^{\perp}$ is more sensitive to a change in the phase Δ_1 than any of the three parameters shown in Figs. 1 for photoionization with the electric vector parallel to the molecular axis.

Figure 2(b) contains the polarization parameter $\kappa^{\perp}$ calculated from Eq. (28b). Although $\kappa^{\perp}$ is positive, its behavior as a function of photon energy is the same as that

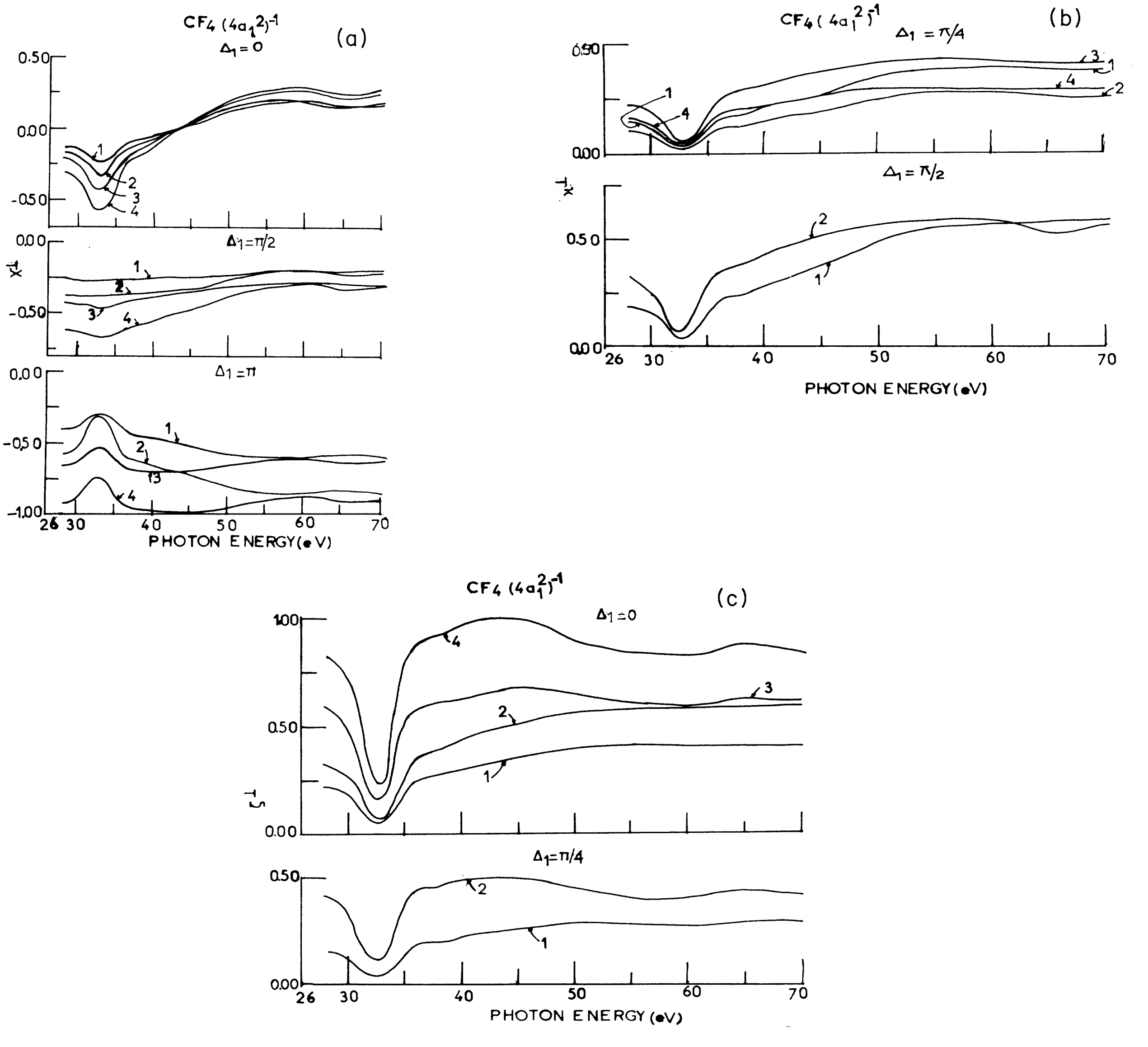

FIG. 2. (a) Variation of $\chi^{\perp}(\mathbf{k})$ with photon energy for ionization in the $4a_1^2$ orbital of CF_4 oriented with its axis perpendicular to the electric vector in the incident light. The $|X_1|$ used in the expression (28a) was obtained by substituting β, measured by Carlson *et al.* (Ref. 40) in Eq. (33). $(\theta,\phi)=(\pi/8,\pi/4)$ for curve 1, $(\pi/8,\pi/2)$ for curve 2, $(\pi/4,\pi/4)$ for curve 3, $(\pi/4,\pi/2)$ for curve 4. (b) Same as (a) but for $\kappa^{\perp}(\mathbf{k})$ calculated from the expression (28b) for $(\theta,\phi)=(\pi/8,0)$ for curve 1, $(\pi/8,\pi/4)$ for curve 2, $(\pi/4,0)$ for curve 3, $(\pi/4,\pi/4)$ for curve 4. On account of (28b), curve 2 and curve 4 for $\Delta_1=\pi/2$ are exactly the same as the respective curve 1 and curve 3 with $\Delta_1=\pi/4$. (c) Same as (a) but for $\zeta^{\perp}(\mathbf{k})$ calculated from the expression (28c) for values of $(\theta,\phi)=(\pi/4,\pi/8)$ for curve 1, $(\pi/4,\pi/4)$ for curve 2, $(\pi/2,\pi/8)$ for curve 3, $(\pi/2,\pi/4)$ for curve 4. Curve 2 and curve 4 for $\Delta_1=\pi/4$ are, respectively, the same as curve 1 and curve 3 at $\Delta_1=0$.

of $\chi^{\perp}$ shown in Fig. 2(a) for $\Delta_1=0$. The $\zeta^{\perp}$, obtained from the relation (28c), is shown in Fig. 2(c).

2. *Photoionization in the $6a_1^2$ orbital of CCl_4*

The values of $\bar{\beta}$ used in Eq. (33) in this case are those measured by Carlson *et al.*[38] for spin-unresolved photoionization in the $6a_1^2$ orbital of randomly oriented molecules of gaseous CCl_4. The energies of the incident radiation considered are from 23 to 55 eV. The $\bar{\beta}$ for all these measurements reported by Carlson *et al.*[38] was much greater than $-\frac{1}{5}$.

The polarization parameters $(\chi^{\parallel},\kappa^{\parallel},\zeta^{\parallel})$ and $(\chi^{\perp},\kappa^{\perp},\zeta^{\perp})$ for photoionization in the $6a_1^2$ orbital of oriented CCl_4 in a coplanar arrangement with molecular axis parallel and perpendicular to the electric vector in the incident light are shown in Figs. 3(a)–3(c) and 4(a)–4(c), respectively. These have been calculated from the respective Eqs. (17a)–(17c) and (28a)–(28c). In all these figures we find that $\chi^{\parallel}$, $\kappa^{\parallel}$, $\zeta^{\parallel}$, $\chi^{\perp}$, $\kappa^{\perp}$, and $\zeta^{\perp}$ are smoothly varying functions of photon energy and do not change much with the phase Δ_1.

Carlson *et al.*,[38] while analyzing their ARPES for ionization in the $6a_1^2$ orbital of unoriented CCl_4, had con-

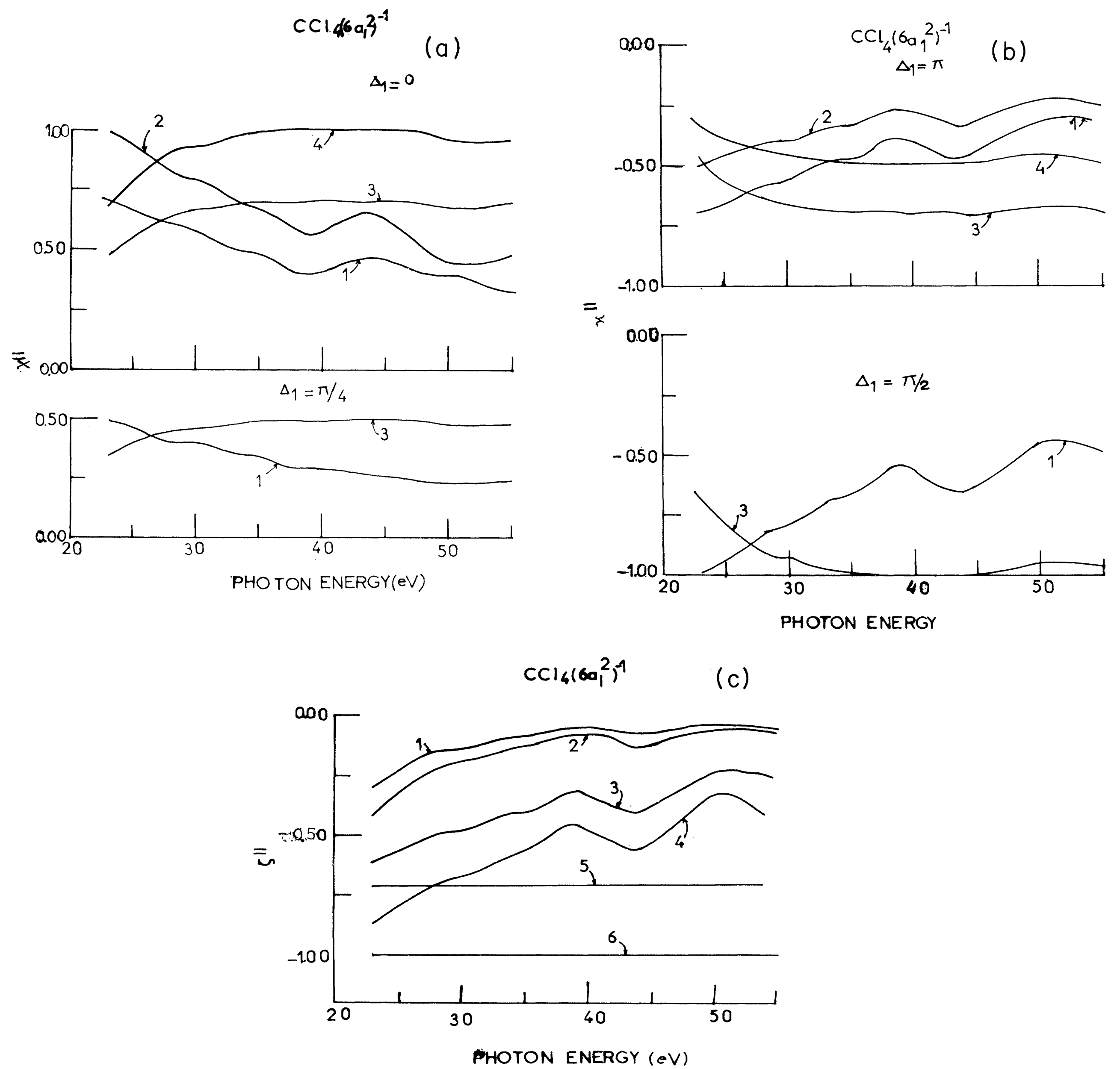

FIG. 3. Parts (a)–(c) are, respectively, the same as those of Fig. 1 but for photoionization in the $6a_1^2$ orbital of CCl_4. The $|X_1|$ used in the respective expressions (17a)–(17c) was obtained by substituting $\bar{\beta}$, measured by Carlson *et al.* (Ref. 38), in Eq. (33).

cluded that there is a nonzero minimum, called the Cooper minimum,[44] in the integrated partial cross section $\bar{\sigma}$ for ionization by about 45 eV photons. In our angle- and spin-resolved study of photoionization in $6a_1^2$ orbital of freely rotating CCl_4 in II we found that this minimum was due probably to a vanishing contribution, for photon energies between 43 and 50 eV, of the ionization integral $R_1(e_{5/2})$ associated with the spin-resolved transition $6a_1^2 \rightarrow 6a_1(e_{1/2})kt_2(e_{5/2})$ in CCl_4. It was shown therein[10] that this minimum corresponds to $X_1 \simeq 2$, i.e., $|X_1| \simeq 2$ with $\Delta_1 \simeq 0$, in Eqs. (20) in this paper. On substituting these in (17) we find that

$$\chi^{\parallel}(\mathbf{k}) = \frac{\tan\theta \sin\phi}{1+\frac{1}{4}\tan^2\theta} , \tag{34a}$$

$$\kappa^{\parallel}(\mathbf{k}) = 0 , \tag{34b}$$

and

$$\zeta^{\parallel}(\mathbf{k}) = -\frac{1}{4}\,\frac{\tan^2\theta \sin 2\phi}{1+\frac{1}{4}\tan^2\theta} \tag{34c}$$

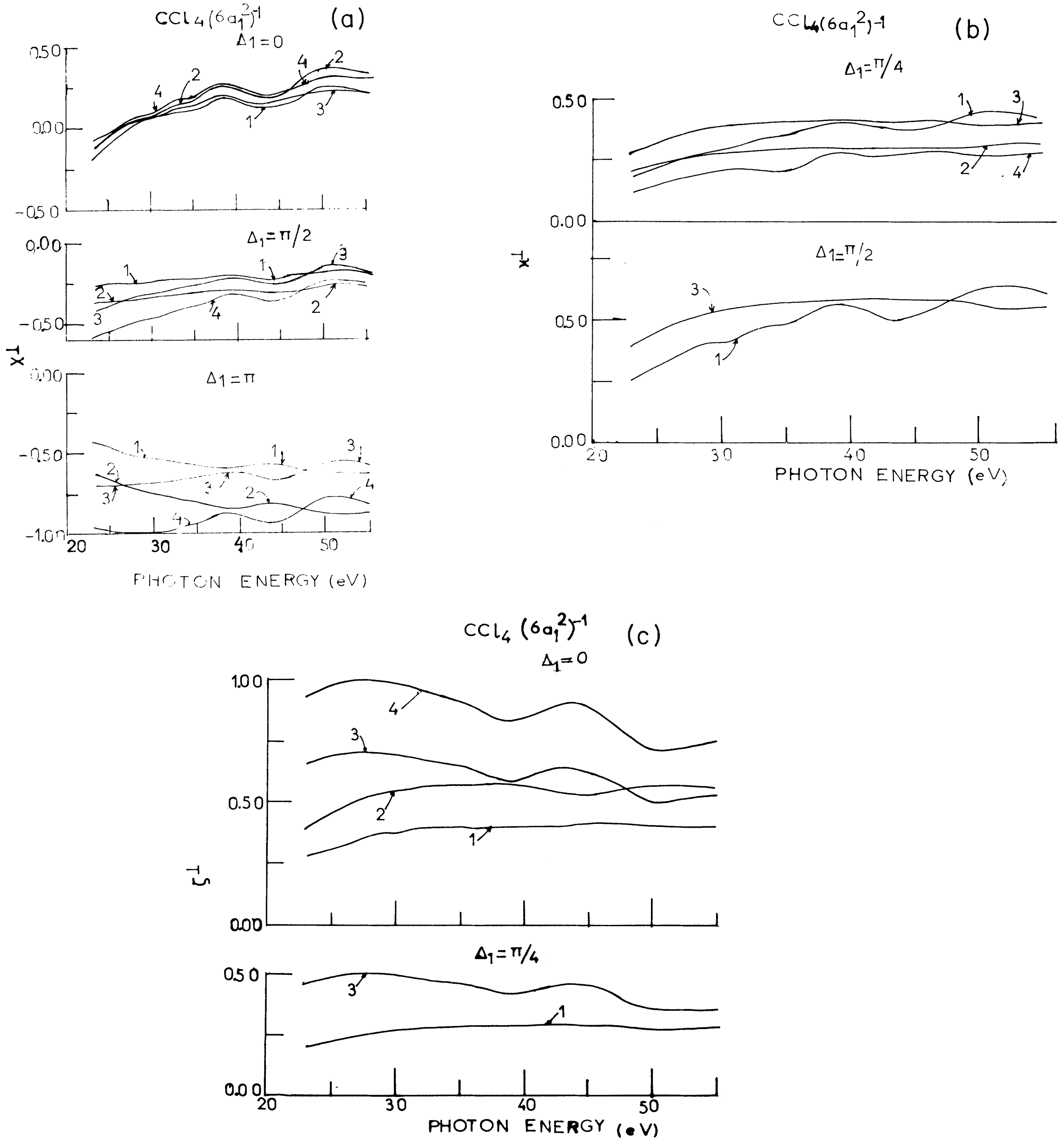

FIG. 4. Parts (a)–(c) are, respectively, the same as those of Fig. 2 but for photoionization in the $6a_1^2$ orbital of CCl_4. The $|X_1|$ used in the respective Eqs. (28a)–(28c) was obtained by substituting $\bar{\beta}$, measured by Carlson *et al.* (Ref. 38), in Eq. (33).

for ionization with the electric vector parallel to the $\mathrm{CCl_4}$ axis. If the electric vector, on the other hand, is perpendicular to the molecular axis, we find from Eqs. (28) that

$$\chi^{\perp}(\mathbf{k})=\frac{\sin 2\theta \sin\phi}{2+3\sin^2\theta}\ , \tag{35a}$$

$$\kappa^{\perp}(\mathbf{k})=0\ , \tag{35b}$$

and

$$\zeta^{\perp}(\mathbf{k})=4\frac{\sin^2\theta \sin 2\phi}{2+3\sin^2\theta}\ . \tag{35c}$$

The degree of spin polarization of electrons produced by ionization in the $6a_1^2$ orbital of $\mathrm{CCl_4}$ oriented with its axis parallel and perpendicular to the electric vector in the incident light is readily obtained in the region of the Cooper minimum[44] by substituting the parameters (34a)–(34c) in (19) and (35a)–(35c) in (27). The degree of spin polarization in neither of these cases is necessarily zero and depends very strongly upon the direction $\mathbf{k}(\theta,\phi)$ of propagation of photoelectrons. In II we found, on the other hand, that in the case of $\mathrm{CCl_4}(6a_1^2)^{-1}$ ASRPES of a freely rotating molecule in the region of the Cooper minimum, only the electrons ejected by the circularly polarized light were spin resolved, whereas those produced by the interaction of the target with a linearly polarized or unpolarized photon beam had no spin selection.

3. Photoionization in the $7a_1^2$ orbital or $SiCl_4$

Carlson *et al.*[42] have taken ARPES of the $7a_1^2$ orbital in unoriented $\mathrm{SiCl_4}$. The values of $\bar\beta$ measured by them were always greater than $-\frac{1}{5}$ over the whole range of energy (19–80 eV) considered in their experiment.[42] Those measurements[42] of $\bar\beta$ can be used again in Eq. (33) to calculate $|X_1|$ needed to study the angle- and spin-resolved photoionization from Eqs. (17) and (28) also in the $7a_1^2$ orbital of $\mathrm{SiCl_4}$ oriented with its axis parallel and perpendicular to the electric vector in the incident light, respectively.

While studying the angular distribution of spin-polarized electrons ejected from the $7a_1^2$ orbital of a freely rotating $\mathrm{SiCl_4}$ in II, we had found that the nonzero minimum[44] observed by Carlson *et al.*[42] between 38 and 45 eV in the spin-unresolved $(7a_1^2)^{-1}$ photoelectron spectrum of unoriented $\mathrm{SiCl_4}$ is due probably to a vanishing contribution of the ionization integral $R_1(g_{3/2})$ associated with the spin-resolved transition $7a_1^2 \rightarrow 7a_1(e_{1/2})kt_2(g_{3/2})$ in $\mathrm{SiCl_4}$ giving $X_1 \simeq -1$, i.e., $|X_1|\simeq 1$ and $\Delta_1 \simeq \pi$, in Eqs. (20).

In order to obtain the polarization parameters in the region of the Copper minimum for ionization in the $7a_1^2$ orbital of $\mathrm{SiCl_4}$ oriented with its axis parallel and perpendicular to the electric vector in the photon beam, we substitute these values of $|X_1|$ and Δ_1 in Eqs. (17) and (28), respectively:

$$\chi^{\parallel}(\mathbf{k})=\chi^{\perp}(\mathbf{k})=-\sin 2\theta \sin\phi\ , \tag{36a}$$

$$\kappa^{\parallel}(\mathbf{k})=\kappa^{\perp}(\mathbf{k})=0\ , \tag{36b}$$

and

$$\zeta^{\parallel}(\mathbf{k})=\zeta^{\perp}(\mathbf{k})=-\sin^2\theta \sin 2\phi\ . \tag{36c}$$

By substituting the parameters (36a)–(36c) in the relations (19) and (27), one finds that the degrees of spin polarization of electrons, ejected from the $7a_1^2$ orbital of $\mathrm{SiCl_4}$ by ionization with the electric vector in the incident light whether parallel or perpendicular to the axis of the oriented molecule, is not zero in general in the region of the Cooper minimum. They instead depend, in both cases, upon the direction of propagation of the photoelectrons and are also equal. It has already been reported in II that, similar to the case of $\mathrm{CCl_4}(6a_1^2)^{-1}$ ASRPES of unoriented target, the angularly distributed photocurrent from the $7a_1^2$ orbital of freely rotating $\mathrm{SiCl_4}$ was spin resolved in the region of the Cooper minimum if the ionizing radiation was circularly polarized. The degree of spin polarization was zero in this case as well if the electrons were ejected by linearly polarized or unpolarized light.

IV. CONCLUSION

In this paper we have applied the theory for ASRPES of oriented molecules, developed in Refs. 9 and 31, to study the $a_1 \rightarrow kt_2$ photoionizing transition in those targets whose point symmetry group is T_d. The spin polarization of photoelectrons in this case is due directly to the SOI in the continuum t_2 orbital of the target. The explicit expressions for the four parameters needed to describe the angular distribution of spin-resolved photoelectrons are obtained. These are for the coplanar experimental configuration (i.e., $\omega=\omega_0$), where the polar axis of the photon-frame, electron-detection directions, and the molecular axis lie in the same plane. The expression for each parameter reduces to very simple forms if one assumes that only the first $l_b=0$ term is taken into account in the single-center expansion (II.2) of $e_{1/2}$ spin-orbital of the bound electron and the photoelectron in both of the two continuum channels $e_{5/2}$ and $g_{3/2}$ is represented by a p $(l=1)$ partial wave only. The resulting relations are then written in yet another form using a complex quantity X_1, already introduced in Ref. 10. The properties of the two sets of parameters $(\chi^{\parallel},\kappa^{\parallel},\zeta^{\parallel})$ and $(\chi^{\perp},\kappa^{\perp},\zeta^{\perp})$, needed to calculate the degree of spin polarization of electrons ejected by ionization in the a_1 orbital of a T_d target with the electric vector parallel and perpendicular to the molecular axis, respectively, are discussed.

These formulas are applied to photoionization in the $4a_1^2$, $6a_1^2$, and $7a_1^2$ orbital of $\mathrm{CF_4}$, $\mathrm{CCl_4}$, and $\mathrm{SiCl_4}$, respectively. Although the magnitude $|X_1|$ of X_1 is extracted from the measurements on $\bar\beta$ using an expression derived in Ref. 10, a knowledge of $\kappa^{\parallel}$ or $\kappa^{\perp}$ is necessary to determine both the sign and the magnitude of the phase Δ_1 of X_1. In order to make simple qualitative predictions for the three examples considered in this paper, we treat Δ_1 (which depends upon the phases of the two dipole matrix elements, phase shifts of the partial waves representing the photo-electron, and is influenced also by the SOI in the continuum part of the molecular spectrum) as a parameter. Because $\zeta^{\parallel}$ does not involve the phase Δ_1, the results presented therefore describe its energy-dependent behavior. By using the values of X_1 (both of the magnitude $|X_1|$ and phase Δ_1) obtained in II, we have also been able to predict the approximate values of the parameters $(\chi^{\parallel},\kappa^{\parallel},\zeta^{\parallel})$ and $(\chi^{\perp},\kappa^{\perp},\zeta^{\perp})$ in the region of the Cooper minima for ionization in the $6a_1^2$ orbital of CCl_4 and the $7a_1^2$ orbital of $SiCl_4$ with the electric vector in the ionizing radiation both parallel and perpendicular to the axis of the oriented targets.

It is, however, possible that in order to take properly into account the energy-dependent effects and the anisotropic final-state interaction, one needs to do dynamical calculations involving both many-electron forces, the values of $l_b > 0$ in the single-center expansion (II.2) of the $e_{1/2}$ spin-orbital, and represent the photoelectron by partial waves higher than p. But such studies for complex nonlinear oriented targets, like those belonging to a T_d point group, will be prohibitively arduous. This communication, along with its companion papers Refs. 9, 10, and 31, presents a methodology for performing such *ab initio* or semiempirical calculations. In this respect, the various formulas derived herein set a framework for the analysis of measurements and computation of the angle- and spin-resolved photoelectron spectrum in a T_d molecule oriented in space.

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