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Photoelectron spectroscopic studies of polyatomic molecules: Spin-polarized electrons from T_d point symmetry group molecules

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This paper presents a study of angle- and spin-resolved photoelectron spectroscopy in a randomly oriented nonlinear molecule in the nonrelativistic, electric dipole approximation. The theory formulated in the preceding paper has been used along with the methods of the extended point (or spin-double) group to develop, perhaps in their simplest possible forms, the expressions for the five parameters needed to specify the angular distribution of spin-polarized electrons ejected in photoionization by unpolarized, or by linearly or circularly polarized light in the a_1 orbital of a T_d molecule. The polarization of the photoelectrons in this case is due directly to the spin-orbit interaction in molecular continua. Such angle- and spin-resolved studies will therefore provide more stringent tests of theoretical models, probes of 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 here set a methodology and a framework for the analysis of measurements and calculations of spin-resolved spectra in nonlinear systems in general and T_d molecules in particular. The specific examples treated in this paper are those of photoionization in the respective $4a_1^2$, $6a_1^2$, and $7a_1^2$ orbitals of unoriented CF_4, CCl_4, and $SiCl_4$ molecular targets. Without any dynamical calculations, and by use instead of the experimentally measured values of the angular asymmetry ($\bar{\beta}$) as a function of the photon wavelength, the variations in $\bar{\xi}$, $\bar{\delta}-\bar{\gamma}$, and $2\bar{\gamma}+\bar{\delta}$ with respect to the energy of the incident radiation and to the phases involved have been studied in detail. These three quantities (where $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\xi}$ are the spin parameters) determine the degree of spin polarization of photoelectrons in various experimental configurations. While $\bar{\delta}-\bar{\gamma}$ is found to be independent of phase, both $\bar{\xi}$ and $2\bar{\gamma}+\bar{\delta}$ depend very strongly upon it. The phase, in turn, is influenced by the spin-orbit interaction. This study has helped also in analyzing and revealing the nature of the Cooper minima observed in $CCl_4(6a_1^2)^{-1}$ and $SiCl_4(7a_1^2)^{-1}$ spectra and in predicting the values of the spin parameters $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\xi}$ in the corresponding energy regions.

I. INTRODUCTION

Recent[1-4] experimental studies have shown that an electron can be spin polarized even if ejected from a randomly oriented molecule due to photoionization by unpolarized or linearly or circularly polarized light. This spin resolution of photoelectrons arises due to the influence of the spin-orbit interaction (SOI) on the ground, ionic, or the continuum state of the molecular target. Because the degree of polarization of an ejected electron depends also on its direction of propagation, the photoemission experiments measuring the spin polarization have therefore to be performed both angle and spin resolved.

The spin-unresolved photoelectron angular distributions are already known to have dependence upon the phase shifts of the various partial waves which describe the outgoing electron and to give information on the phase of the ionization matrix elements, rather than just their absolute squares. The angular distributions of spin-detected photoelectrons will therefore provide additional information about the influence of the SOI upon photoionization dynamics and also stringent tests of theoretical models used for such studies.

The techniques[1] of angle-, energy-, and spin-resolved photoelectron spectroscopy have been applied very successfully to photoionization in both linear (CO_2,N_2O),[2] (Br_2,I_2),[4] and nonlinear (CH_3Br),[3,4] (CH_3I)[4] unoriented molecules. The spin-polarization parameters for HI and HBr diatomics have been calculated by Lefebvre-Brion *et al.*[5] and by Raseev *et al.*[6] by the use of, and if necessary the extention of[6] the theories developed by Cherepkov[7,8] for linear molecular systems.

Hitherto, there have probably been no calculations of angle- and spin-resolved photoelectron spectroscopy (ASRPES) for nonlinear targets. In this paper we report the results of a first theoretical study of angular distribution of spin-resolved electrons produced by photoionization in the respective $4a_1^2$, $6a_1^2$, and $7a_1^2$ orbitals of unoriented CF_4, CCl_4, and $S1Cl_4$ molecules which transform according to the T_d point symmetry group.

The present study is based on the general multichannel theory of ASRPES in nonlinear molecules developed in the preceding article.[9] (A short account of this work has earlier been reported elsewhere.[10]) In this paper we show how the application of this theory,[9] along with the concepts of extended point (or spin double) groups,[11-13] simplifies a formidable problem 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 a_1 orbital in T_d molecules, on the very first application of the group-theoretical methods to those continuum processes in nonlinear molecular systems where SOI is taken into account.

In Sec. II we first determine the double-valued irreducible representations (IR's)[11–13] of the molecular orbitals participating in the photoionization process of interest on the inclusion of SOI with the spin $s=\frac{1}{2}$. The wave functions for the bound and continuum spin orbitals are then written in terms of the basis functions[13–15] of these IR's. Section III contains the calculations of the photoionization matrix elements in the electric dipole ($E1$) length approximation.

It has already been shown in the preceding paper[9] that the angular momentum transfer treatment considerably simplifies formulas for ASRPES in nonlinear molecules. In order to be able to use these expressions, it is, however, necessary to know "reduced" matrix elements for photoionization. In Sec. IV we show how these amplitudes can be calculated from the transition moments obtained in the last section and subsequently be used to obtain explicit expressions for the five parameters ($\overline{\sigma}$, $\overline{\beta}$, $\overline{\gamma}$, $\overline{\delta}$, and $\overline{\xi}$) needed[9] to specify the angular distribution of spin-resolved photoelectrons. These formulas will provide a framework for the analysis of measurements and calculations of ASRPES of the a_1 orbital in T_d molecules.

The magnitude and phase of all the transition moments involved in the formulas obtained in Sec. IV are left as parameters. Section V A shows, on the other hand, that by introducing certain approximations, the five expressions can be simplified to the point where knowledge of any two of the four quantities ($\overline{\beta}$, $\overline{\gamma}$, $\overline{\delta}$, and $\overline{\xi}$) is sufficient to determine the other two and to calculate the magnitudes and the relative phase of the two transition amplitudes involved. The validity of the approximations and the properties of the resulting expressions are also discussed in the Sec. V A.

Section V B contains results on spin-resolved photoelectron angular distribution for ionization in the highest valance a_1 orbital of unoriented CF_4, CCl_4, and $SiCl_4$ by unpolarized and linearly and circularly polarized light. Using the experimentally measured values of $\overline{\beta}$ as a function of the photon wavelength, the variations of $\overline{\xi}$, $\overline{\delta}-\overline{\gamma}$, and $2\overline{\gamma}+\overline{\delta}$ with respect to the energy of the ejected electron and also to the phase (which is treated as a parameter) are studied in detail. The three quantities $\overline{\xi}$, $\overline{\delta}-\overline{\gamma}$, and $2\overline{\gamma}+\overline{\delta}$ determine[9] the degree of spin polarization of the photocurrent produced by the incident radiation in various experimental configurations.

Section V B contains also an interpretation of the Cooper minima[16] observed in ionization in $6a_1^2$ orbital[17] of CCl_4 and in $7a_1^2$ orbital[18] of $SiCl_4$. In addition to predicting the approximate values of $\overline{\beta}$, $\overline{\gamma}$, $\overline{\delta}$, and $\overline{\xi}$, this subsection indicates the transitions whose contributions to photoionization are likely to vanish in the observed energy region of nonzero cross-section minima in the two spectra.[17,18] The conclusions of this study are presented in Sec. VI.

II. MOLECULAR ORBITALS

In order to calculate the spin-resolved photoelectron angular distribution [as defined in Eq. (I.35) of Paper I],[19] we need to know the $E1$ transition amplitudes $d_{hl\nu,b}^{p\tau}(\lambda_r)$ as defined in Eq. (17) of I. [Unless specified otherwise, all the symbols used in this paper have meanings explained in I. References to equations therein will be listed with a I, e.g., Eq. (I.17) means Eq. (17) of the preceding paper.[9]] Let us make two assumptions: (i) The initial state $|\Psi_b\rangle$ and the channel functions $|\Psi_{hl\nu}^{p\tau-}\rangle$ are each represented by a single Slater determinant consisting of only one electron spin orbital expanded about the center of mass of the molecule in the body-fixed frame of reference; (ii) the one-electron states not directly involved in the photoionizing transition remain unchanged, i.e., neglect the core-relaxation effects. The matrix [as defined in Eq. (17) of paper I] then becomes the one-electron dipole integral

$$d_{hl\nu,b}^{p\tau}(\lambda_r)=A^{(a)}\int F_{hl\nu}^{p\tau-}(\hat{\xi}_{\lambda_r}\cdot\mathbf{Q}^{(a)})\psi_b d\mathbf{x} , \qquad (1)$$

where integration over the space and summation over the spin variables (both collectively denoted by $\mathbf{x}$) has to be carried out. In (1)

$$\psi_b(\mathbf{x})=\Phi(\nu_b)r^{-1}\sum_{h_b,l_b}\phi_{h_bl_b}^{p_b}(r)X_{h_bl_b}^{p_b\tau_b}(\hat{\mathbf{r}}) \qquad (2)$$

is the bound spin orbital in which photoionization takes place and $F_{hl\nu}^{p\tau-}$ is the continuum spin orbital of the ejected electron, as defined in Eq. (5) of Paper I.

The selection rules for photoionization in nonlinear molecules in the $E1$ approximation in the absence of SOI, when no measurements of the spin of the ejected electron are made, have already been discussed by us.[20] Accordingly, the continuum orbital of the photoelectron ejected from the nondegenerate a_1 orbital in a T_d molecule should belong to the triply degenerate T_2 IR of this point group.[21]

All the electronic shells in molecular systems like CF_4, CCl_4, $SiCl_4$, etc. are completely filled. The SOI in the initial electronic state $|\Psi_b\rangle$ of the target is therefore zero. An a_1 orbital in these molecules can contain up to two electrons and corresponds to an s or σ shell in atoms or linear molecules, respectively, where SOI always vanishes. Hence the SOI in the ionic state formed by the loss of an electron in an a_1^2 orbital in T_d molecular targets will be zero as well. On the other hand, the SOI in a singly occupied t_2 orbital of such molecules is certainly present. Consequently, similar to Fano[22] effect in ns^1 or ns^2 atomic shells,[8,23] the spin polarization of photoelectrons ejected from a_1 orbital in a randomly oriented T_d molecule will be due completely to the SOI in the continuum part of the molecular spectrum.

Because the total spin in the continuum t_2 orbital is 1/2 (i.e., half integer), in order to describe the SOI properly, one therefore needs to consider the extended T_d point group.[11–13] The spin-$\frac{1}{2}$ functions transform according to the $E_{1/2}$ double-valued IR of this extended group.[11–13] [Here, and in the following, we have used the notations discussed by Herzberg[11] and by Bunker[12] for spin-double (extended) point group.] Therefore, the symmetries of the bound and continuum molecular orbitals, when the SOI with $s=\frac{1}{2}$ is also taken into account for studying the spin polarization of photoelectrons, are given by the direct products $A_1 \otimes E_{1/2} = E_{1/2}$ and $T_2 \otimes E_{1/2} = E_{5/2} \oplus G_{3/2}$ of the extended T_d group. Hence an electron photoionization from a_1^2 bound orbital has available to it two continuum channels which belong to the $E_{5/2}$ and $G_{3/2}$ double-valued IR's of the extended group of a T_d molecule. The corresponding bound-free transitions are therefore

$$a_1^2 \to a_1^1\,(e_{1/2})kt_2(e_{5/2})$$

and

$$a_1^2 \to a_1^1\,(e_{1/2})kt_2(g_{3/2})\ ,$$

respectively. Here, while both $E_{1/2}$ and $E_{5/2}$ are doubly degenerate, $g_{3/2}$ is a quadruply degenerate IR.

Cracknell[13,14] and Cracknell and Joshua[15] have developed symmetry-adapted basis functions for the double-valued IR's of most of the 32 extended point groups. For the sake of convenience in the present study, we write these functions in the following form

$$\chi_{hl}^{(p)q\iota}(\mathbf{x}) = \sum_{\tau,\nu} a_\nu^{(p\tau)q\iota} X_{hl}^{p\tau}(\hat{\mathbf{r}})\Phi(\nu)\ . \tag{3}$$

Here $X_{hl}^{p\tau}$ [or, $X_{h_b l_b}^{p_b \tau_b}$ in Eq. (2)], [already explained in Eq. (6) of Paper I], is a GH for the pth single-valued IR of a point group in the absence of SOI. The superscript q denotes one of the double-valued representations which is associated with the pth IR of this point group. The symbol ι stands for the dimensionality, i.e., degeneracy of the qth IR of the extended group. The interesting thing to note here is that the two associated single- and double-valued IR's of a point group have same number [denoted by the subscript h in the expansion (3)] of different basis for the same l.

The basis functions developed by Cracknell[13,14] and by Cracknell and Joshua[15] are orthonormal, i.e.,

$$\int [\chi_{hl}^{(p)q'\iota'}(\mathbf{x})]^* \chi_{hl}^{(p)q\iota}(\mathbf{x})\,d\mathbf{x} = \delta_{qq'}\delta_{\iota\iota'} \tag{4}$$

and satisfy the completeness relation

$$\sum_{q,\iota} [\chi_{hl}^{(p)q\iota}(\mathbf{x}')]^* \chi_{hl}^{(p)q\iota}(\mathbf{x}) = \delta(\mathbf{x}-\mathbf{x}')\ . \tag{5}$$

One can then show that the expansion coefficients in (3) are such that

$$\sum_{\tau,\nu} (a_\nu^{(p\tau)q'\iota'})^* a_\nu^{(p\tau)q\iota} = \delta_{qq'}\delta_{\iota\iota'} \tag{6}$$

and

$$\sum_{q,\iota} (a_{\nu'}^{(p\tau')q\iota})^* a_\nu^{(p\tau)q\iota} = \delta_{\tau\tau'}\delta_{\nu\nu'}\ . \tag{7}$$

Also, a relation inverse to (3) is

$$X_{hl}^{p\tau}(\hat{\mathbf{r}})\Phi(\nu) = \sum_{q,\iota} (a_\nu^{(p\tau)q\iota})^* \chi_{hl}^{(p)q\iota}(\mathbf{x})\ . \tag{8}$$

The symmetry-adapted basis functions for the double-valued IR's of an extended T_d point group of interest in the present and in our planned future[24] articles are given in the Appendix in this paper.

One can now expand both the bound and the continuum spin orbitals (2) and (I.5), respectively, in terms of the basis functions of the double-valued IR's of the extended point group of the target molecule. We therefore write, in view of the relation (8),

$$\psi_b(\mathbf{x}) = r^{-1} \sum_{q_b,\iota_b,h_b,l_b} (a_{\nu_b}^{(p_b\tau_b)q_b\iota_b})^* \phi_{h_b l_b}^{q_b}(r)\chi_{h_b l_b}^{(p_b)q_b\iota_b}(\mathbf{x})\ , \tag{9}$$

and

$$F_{hl\nu}^{p\tau -}(\mathbf{x}) = r^{-1} \sum_{q,\iota,h',l'} (a_\nu^{(p\tau)q\iota})^* U_{hl,h'l'}^{q-}(r) X_{h'l'}^{(p)q\iota}(\mathbf{x})\ , \tag{10}$$

with

$$\lim_{r\to\infty} U_{hl,h'l'}^{q-}(r) = i\left[\frac{m_e}{2\pi\hbar^2 k}\right]^{1/2} [e^{-i\theta_{l'}}(S^q)_{hl,h'l'}^\dagger - e^{i\theta_l}\delta_{hh'}\delta_{ll'}]\ , \tag{11}$$

analogous to the incoming-wave asymptotic wave boundary conditions [Eq. (I.7)] satisfied by the radial part of the wave function of the ejected electron. On substituting the expansion (3), the respective bound and continuum spin orbitals (9) and (10) can finally be written in terms of the GH of the single-valued IR's of the molecular point group:

$$\psi_b(\mathbf{x}) = r^{-1} \sum_{\substack{q_b\iota_b,h_b,l_b,\\ \tau_b',\nu_b'}} (a_{\nu_b}^{(p_b\tau_b)q_b\iota_b})^* a_{\nu_b'}^{(p_b\tau_b')q_b\iota_b} \phi_{h_b l_b}^{q_b}(r) \times X_{h_b l_b}^{p_b\tau_b'}(\hat{\mathbf{r}})\Phi(\nu_b') \tag{12}$$

and

$$F_{hl\nu}^{p\tau -}(\mathbf{x}) = r^{-1} \sum_{\substack{q,\iota,h',l'\\ \tau',\nu'}} (a_\nu^{(p\tau)q\iota})^* a_{\nu'}^{(p\tau')q\iota} \times U_{hl,h'l'}^{q-}(r) X_{h'l'}^{p\tau'}(\hat{\mathbf{r}})\Phi(\nu')\ . \tag{13}$$

Both of the results (12) and (13) are exact and in their most general forms. They can be used to obtain bound and continuum molecular spin orbitals participating in a photoionization process in a target of any symmetry belonging to one of the 32 point groups in the presence of SOI.

Let us specialize (12) and (13) to the present example of photoionization in a_1 orbital in a T_d molecule. According to the discussion given after Eq. (2), we obviously have $p_b = a_1$, $q_b = e_{1/2}$, $\iota_b = 2$, and $\nu_b, \nu_{b'} = \pm\frac{1}{2}$. Because the A_1 IR in a T_d molecule is one dimensional and there is always one GH for each value of l in this case,[20] we therefore have $\tau_b, h_b = 1$. The expansion (12) for the bound orbital then becomes

$$\psi_{a_1\nu_b}(\mathbf{x})=r^{-1}\sum_{l_b,\nu_b'}[(a_{\nu_b}^{(a_1)e_{1/2}1})^* a_{\nu_b'}^{(a_1)e_{1/2}1}+(a_{\nu_b}^{(a_1)e_{1/2}2})^* a_{\nu_b'}^{(a_1)e_{1/2}2}]\times\phi_{l_b}^{e_{1/2}}(r)X_{l_b}^{a_1}(\hat{\mathbf{r}})\Phi(\nu_b') \ . \tag{13}$$

On substituting for the coefficients a's from the Appendix, we finally obtain

$$\begin{aligned}\psi_{a_1,1/2}(\mathbf{x})&=\alpha r^{-1}\sum_{l_b}\phi_{l_b}^{e_{1/2}}(r)X_{l_b}^{a_1}(\hat{\mathbf{r}}) \ ,\\ \psi_{a_1,-1/2}(\mathbf{x})&=\beta r^{-1}\sum_{l_b}\phi_{l_b}^{e_{1/2}}(r)X_{l_b}^{a_1}(\hat{\mathbf{r}}) \ .\end{aligned} \tag{14}$$

For the continuum orbital we have, on the other hand, $p=t_2$, $\tau=1-3$, $q=e_{5/2}$, and $g_{3/2}$. Equation (13), therefore, yields

$$F_{hl\nu}^{t_2\tau-}(\mathbf{x})=r^{-1}\sum_{h',l',\iota}\sum_{\tau'=1}^{3}\sum_{\nu'=-1/2}^{1/2}[(a_{\nu}^{(t_2\tau)e_{5/2}\iota})^* a_{\nu'}^{(t_2\tau')e_{5/2}\iota}U_{hl,h'l'}^{e_{5/2}-}(r)+(a_{\nu}^{(t_2\tau)g_{3/2}\iota})^* a_{\nu'}^{(t_2\tau')g_{3/2}\iota}U_{hl,h'l'}^{g_{3/2}-}(r)]X_{h'l'}^{t_2\tau'}(\hat{\mathbf{r}})\Phi(\nu') \ ,$$

where $\iota=1-2$ and $1-4$, respectively, for $E_{5/2}$ and $G_{3/2}$ double-valued IR's of the extended T_d point group. After evaluating the sums over τ', ν', and ι, and substituting for the coefficient a's from the Appendix, we finally obtain the following expressions for the continuum spin orbital of the photoelectron:

$$F_{h,l,1/2}^{t_21-}(\mathbf{x})=\tfrac{1}{3}r^{-1}\sum_{h',l'}\{\alpha[(X_{h'l'}^{t_21}+iX_{h'l'}^{t_22})U_{hl,h'l'}^{e_{5/2}-}+(2X_{h'l'}^{t_21}-iX_{h'l'}^{t_22})U_{hl,h'l'}^{g_{3/2}-}]+\beta X_{h'l'}^{t_23}(U_{hl,h'l'}^{e_{5/2}-}-U_{hl,h'l'}^{g_{3/2}-})\} \ , \tag{15a}$$

$$F_{h,l,-1/2}^{t_21-}(\mathbf{x})=\tfrac{1}{3}r^{-1}\sum_{h'l'}\{\beta[(X_{h'l'}^{t_21}-iX_{h'l'}^{t_22})U_{hl,h'l'}^{e_{5/2}-}+(2X_{h'l'}^{t_21}+iX_{h'l'}^{t_22})U_{hl,h'l'}^{g_{3/2}-}]-\alpha X_{h'l'}^{t_23}(U_{hl,h'l'}^{e_{5/2}-}-U_{hl,h'l'}^{g_{3/2}-})\} \ , \tag{15b}$$

$$F_{h,l,1/2}^{t_22-}(\mathbf{x})=\tfrac{1}{3}r^{-1}\sum_{h',l'}\{\alpha[(X_{h'l'}^{t_22}-iX_{h'l'}^{t_21})U_{hl,h'l'}^{e_{5/2}-}+(2X_{h'l'}^{t_22}+iX_{h'l'}^{t_21})U_{hl,h'l'}^{g_{3/2}-}]-i\beta X_{h'l'}^{t_23}(U_{hl,h'l'}^{e_{5/2}-}-U_{hl,h'l'}^{g_{3/2}-})\} \ , \tag{15c}$$

$$F_{h,l,-1/2}^{t_22-}(\mathbf{x})=\tfrac{1}{3}r^{-1}\sum_{h',l'}\{\beta[(X_{h'l'}^{t_22}+iX_{h'l'}^{t_21})U_{hl,h'l'}^{e_{5/2}-}+(2X_{h'l'}^{t_22}-iX_{h'l'}^{t_21})U_{hl,h'l'}^{g_{3/2}-}]-i\alpha X_{h'l'}^{t_23}(U_{hl,h'l'}^{e_{5/2}-}-U_{hl,h'l'}^{g_{3/2}-})\} \ , \tag{15d}$$

$$F_{h,l,1/2}^{t_23-}(\mathbf{x})=\tfrac{1}{3}r^{-1}\sum_{h',l'}[\beta(X_{h'l'}^{t_21}-iX_{h'l'}^{t_22})(-U_{hl,h'l'}^{e_{5/2}-}+U_{hl,h'l'}^{g_{3/2}-})+\alpha X_{h'l'}^{t_23}(U_{hl,h'l'}^{e_{5/2}-}+2U_{hl,h'l'}^{g_{3/2}-})] \ , \tag{15e}$$

$$F_{h,l,-1/2}^{t_23-}(\mathbf{x})=\tfrac{1}{3}r^{-1}\sum_{h',l'}[\alpha(X_{h'l'}^{t_21}+iX_{h'l'}^{t_22})(U_{hl,h'l'}^{e_{5/2}-}-U_{hl,h'l'}^{g_{3/2}-})+\beta X_{h'l'}^{t_23}(U_{hl,h'l'}^{e_{5/2}-}+2U_{hl,h'l'}^{g_{3/2}-})] \ . \tag{15f}$$

No approximations are involved in the derivations of the bound and continuum spin orbitals (14) and (15), respectively. Both of these are therefore exact.

III. DIPOLE MATRIX ELEMENTS

The one-electron integral (1) for the photoionization matrix element takes the following form:

$$d_{hl\nu,b}^{t_2\tau}(\lambda_r)=A^{(1)}\left[\frac{4\pi}{3}\right]^{1/2}\langle F_{hl\nu}^{t_2\tau-}|rY_1^{\lambda_r}|\psi_{a_1\nu_b}\rangle$$

in the $E1$ length approximation.[25,26] This integral can be evaluated by substituting any of the two bound and continuum orbitals (12) or (14), and (13) or (15), respectively. In the present case, it will, however, be convenient if we use (13) for $F_{hl\nu}^{t_2\tau-}$ and (14) for $\psi_{a_1\nu_b}$. Because the spin functions α and β are orthonormal, we therefore obtain

$$d_{hl\nu,\nu_b}^{t_2\tau}(\lambda_r)=\left[\frac{4\pi}{3}\right]^{1/2}A^{(1)}\sum_{h',l',\tau'}\sum_{q,\iota,l_b}a_{\nu}^{(t_2\tau)q\iota}(a_{\nu_b}^{(t_2\tau')q\iota})^*\langle X_{h'l'}^{t_2\tau'}|Y_1^{\lambda_r}|X_{l_b}^{a_1}\rangle\int_0^{\infty}U_{hl,h'l'}^{q-}(r)r\phi_{l_b}^{e_{1/2}}(r)dr \ .$$

Remembering[20] that $h,h'=1$ for GH belonging to the t_2 IR in T_d molecules with $l,l'\leq 4$, and substituting the expansion (I.6) for $X_{h'l'}^{t_2\tau'}$ and $X_{l_b}^{a_1}$, the transition moment becomes

$$d_{l\nu,\nu_b}^{t_2\tau}(\lambda_r)=\left[\frac{4\pi}{3}\right]^{1/2}\sum_{\substack{l',m',\\ l_b,m_b}}\sum_{\tau',q,\iota}a_{\nu}^{(t_2\tau)q\iota}(a_{\nu_b}^{(t_2\tau')q\iota})^* b_{l_bm_b}^{a_1}(b_{l'm'}^{t_2\tau'})^*\langle Y_{l'}^{m'}|Y_1^{\lambda_r}|Y_{l_b}^{m_b}\rangle I_{ll',l_b}^{q-} \ , \tag{16}$$

where

$$I_{ll',l_b}^{q-}=A^{(1)}\int_0^{\infty}U_{ll'}^{q-*}(r)r\phi_{l_b}^{e_{1/2}}(r)dr \tag{17}$$

is the radial dipole integral.

In order to proceed further, it is necessary to specify the values of l_b in (16). In the present study, only the two lowest of the permitted values,[20] $l_b=0$ and 3, are considered. Extension to still higher values of l_b is straightforward. Then the allowed values of l' so that the angular integral over the three spherical harmonics present in (16) does not identically vanish, are (1) and (2), (4) for $l_b=0$ and $l_b=3$, respectively. Using the expansion coefficients $b_{l_b m_b}^{a_1}$ and $b_{lm}^{t_2\tau}$ for GH from Appendix 3 in Ref. 20, we obtain following expressions:

$$\begin{aligned} d_{l,\nu;1/2}^{t_2\tau}(\lambda_r)= & -\frac{1}{\sqrt{3}}\delta_{0\lambda_r}[a_\nu^{(t_2\tau)e_{5/2}1}R_l(1;e_{5/2})-\sqrt{2}a_\nu^{(t_2\tau)g_{3/2}2}R_l(1;g_{3/2})] \\ & +\frac{1}{\sqrt{6}}(\delta_{-1\lambda_r}-\delta_{1\lambda_1})\left[a_\nu^{(t_2\tau)e_{5/2}2}R_l(1;e_{5/2})+\sqrt{3/2}\left[a_\nu^{(t_2\tau)g_{3/2}3}+\frac{1}{\sqrt{3}}a_\nu^{(t_2\tau)g_{3/2}4}\right]R_l(1;g_{3/2})\right] \\ & +\frac{i}{\sqrt{6}}(\delta_{-1\lambda_r}+\delta_{1\lambda_r})\left[a_\nu^{(t_2\tau)e_{5/2}2}R_l(2;e_{5/2})-\sqrt{3/2}\left[a_\nu^{(t_2\tau)g_{3/2}3}-\frac{1}{\sqrt{3}}a_\nu^{(t_2\tau)g_{3/2}4}\right]R_l(2;g_{3/2})\right] , \end{aligned} \tag{18a}$$

for $\nu_b=+\frac{1}{2}$ and

$$\begin{aligned} d_{l,\nu;-1/2}^{t_2\tau}(\lambda_r)= & \frac{1}{\sqrt{3}}\delta_{0\lambda_r}[a_\nu^{(t_2\tau)e_{5/2}2}R_l(1;e_{5/2})-\sqrt{2}a_\nu^{(t_2\tau)g_{3/2}4}R_l(1;g_{3/2})] \\ & +\frac{1}{\sqrt{6}}(\delta_{-1\lambda_r}-\delta_{1\lambda_r}\left[a_\nu^{(t_2\tau)e_{5/2}1}R_l(1;e_{5/2})+\sqrt{3/2}\left[a_\nu^{(t_2\tau)g_{3/2}1}+\frac{1}{\sqrt{3}}a_\nu^{(t_2\tau)g_{3/2}2}\right]R_l(1;g_{3/2})\right] \\ & -\frac{i}{\sqrt{6}}(\delta_{-1\lambda_r}+\delta_{1\lambda_r})\left[a_\nu^{(t_2\tau)e_{5/2}1}R_l(2;e_{5/2})-\sqrt{3/2}(a_\nu^{(t_2\tau)g_{3/2}1}-\frac{1}{\sqrt{3}}a_\nu^{(t_2\tau)g_{3/2}2})R_l(2;g_{3/2})\right] , \end{aligned} \tag{18b}$$

for $\nu_b=-\frac{1}{2}$. Here

$$R_l(1;q)=\frac{1}{\sqrt{3}}I_{l1,0}^{q-}+\frac{1}{\sqrt{7}}I_{l2,3}^{q-}-\frac{2}{\sqrt{21}}I_{l4,3}^{q-} , \tag{19a}$$

$$R_l(2;q)=\frac{1}{\sqrt{3}}I_{l1,0}^{q-}-\frac{1}{\sqrt{7}}I_{l2,3}^{q-}+\frac{2}{\sqrt{21}}I_{l4,3}^{q-} , \tag{19b}$$

are the $E1$ ionization integrals.

Taking $\tau=1-3$ and $\nu=\pm\frac{1}{2}$ in (18), we finally obtain the 12 ionization amplitudes

$$d_{l,1/2;1/2}^{\tau=1}(\lambda_r)=\frac{1}{3\sqrt{2}}\{\delta_{-1\lambda_r}[R_l(1+)-iR_l(2-)]-\delta_{1\lambda_r}[R_l(1+)+iR_l(2-)]\} , \tag{20a}$$

$$d_{l,-1/2;1/2}^{\tau=1}(\lambda_r)=-d_{l,1/2;-1/2}^{\tau=1}(\lambda_r)=\tfrac{1}{3}\delta_{0\lambda_r}R_l(1-) , \tag{20b}$$

$$d_{l,-1/2;-1/2}^{\tau=1}(\lambda_r)=\frac{1}{3\sqrt{2}}\{\delta_{-1\lambda_r}[R_l(1+)+iR_l(2-)]-\delta_{1\lambda_r}[R_l(1+)-iR_l(2-)]\} , \tag{20c}$$

$$d_{l,1/2;1/2}^{\tau=2}(\lambda_r)=-\frac{1}{3\sqrt{2}}\{\delta_{-1\lambda_r}[R_l(2+)+iR_l(1-)]+\delta_{1\lambda_r}[R_l(2+)-iR_l(1-)]\} , \tag{20d}$$

$$d_{l,-1/2;1/2}^{\tau=2}(\lambda_r)=d_{l,\frac{1}{2};-\frac{1}{2}}^{\tau=2}(\lambda_r)=-i\frac{1}{3}\delta_{0\lambda_r}R_l(1-) , \tag{20e}$$

$$d_{l,-1/2;-1/2}^{\tau=2}(\lambda_r)=-\frac{1}{3\sqrt{2}}\{\delta_{-1\lambda_r}[R_l(2+)-iR_l(1-)]+\delta_{1\lambda_r}[R_l(2+)+iR_l(1-)]\} , \tag{20f}$$

$$d_{l,1/2;1/2}^{\tau=3}(\lambda_r)=d_{l,-1/2,-1/2}^{\tau=3}(\lambda_r)=\tfrac{1}{3}\delta_{0\lambda_r}R_l(1+) , \tag{20g}$$

$$d_{l,-1/2;1/2}^{\tau=3}(\lambda_r)=-\frac{1}{3\sqrt{2}}\{\delta_{-1\lambda_r}[R_l(1-)+iR_l(2-)]-\delta_{1\lambda_r}[R_l(1-)-iR_l(2-)]\} , \tag{20h}$$

$$d_{l,1/2;-1/2}^{\tau=3}(\lambda_r)=\frac{1}{3\sqrt{2}}\{\delta_{-1\lambda_r}[R_l(1-)-iR_l(2-)]-\delta_{1\lambda_r}[R_l(1-)+iR_l(2-)]\} \tag{20i}$$

for each of the three values of $\lambda_r=0,\pm1$. Here we have defined

$$\begin{aligned} R_l(i-)&=R_l(i;g_{3/2})-R_l(i;e_{5/2}) , \\ R_l(i+)&=2R_l(i;g_{3/2})+R_l(i;e_{5/2}) , \end{aligned} \tag{21}$$

with $i=1\text{-}2$, and the superscript $p=t_2$ has not been written on the d's in (20) for brevity. The radial integrals I^{q-} defined in (17) can be the goal of a particular calculational study to obtain the ionization integrals (19), hence the amplitudes (20), by *ab initio* methods. In this paper they will however be treated as parameters.

The structure of the transition moments (20) becomes more transparent if they are written in matrix forms

$$d_l^{\tau=1}(-1)=\frac{1}{3\sqrt{2}}\begin{array}{c}\begin{array}{cc}\nu_b=\frac{1}{2} & \nu_b=-\frac{1}{2}\end{array}\\ \left[\begin{array}{cc}R_l(1+)-iR_l(2-) & 0\\ 0 & R_l(1+)+iR_l(2-)\end{array}\right]\end{array}\begin{array}{l}\\ \nu=\frac{1}{2}\\ \nu=-\frac{1}{2}\ ,\end{array} \tag{22a}$$

$$d_l^{\tau=1}(0)=\tfrac{1}{3}R_l(1-)\begin{bmatrix}0 & -1\\ 1 & 0\end{bmatrix}, \tag{22b}$$

$$d_l^{\tau=1}(+1)=-\frac{1}{3\sqrt{2}}\begin{bmatrix}R_l(1+)+iR_l(2-) & 0\\ 0 & R_l(1+)-iR_l(2-)\end{bmatrix}, \tag{22c}$$

$$d_l^{\tau=2}(-1)=-\frac{1}{3\sqrt{2}}\begin{bmatrix}R_l(2+)+iR_l(1-) & 0\\ 0 & R_l(2+)-iR_l(1-)\end{bmatrix}, \tag{22d}$$

$$d_l^{\tau=2}(0)=-\frac{i}{3}R_l(1-)\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}, \tag{22e}$$

$$d_l^{\tau=2}(+1)=-\frac{1}{3\sqrt{2}}\begin{bmatrix}R_l(2+)-iR_l(1-) & 0\\ 0 & R_l(2+)+iR_l(1-)\end{bmatrix}, \tag{22f}$$

$$d_l^{\tau=3}(-1)=\frac{1}{3\sqrt{2}}\begin{bmatrix}0 & R_l(1-)-iR_l(2-)\\ -[R_l(1-)+R_l(2-)] & 0\end{bmatrix}, \tag{22g}$$

$$d_l^{\tau=3}(0)=\tfrac{1}{3}R_l(1+)\underline{1}\ , \tag{22h}$$

$$d_l^{\tau=3}(+1)=\frac{1}{3\sqrt{2}}\begin{bmatrix}0 & -[R_l(1-)+iR_l(2-)]\\ R_l(1-)-iR_l(2-) & 0\end{bmatrix}, \tag{22i}$$

where $\underline{1}$ is a 2×2 unit matrix in (22h).

In the absence of the SOI, the radial integrals (17) for $I_{ll',l_b}^{e_{5/2}-}$ and $I_{ll',l_b}^{g_{3/2}-}$ will be equal, i.e.,

$$I_{ll',l_b}^{e_{5/2}-}=I_{ll',l_b}^{g_{3/2}-}\equiv I_{ll',l_b}^{-}\ . \tag{23}$$

We then obtain from (19)

$$\begin{aligned}R_l(1;e_{5/2})&=R_l(1;g_{3/2})\\ &\equiv R_l(1)\\ &=\frac{1}{\sqrt{3}}I_{l1,0}^{-}+\frac{1}{\sqrt{7}}I_{l2,3}^{-}-\frac{2}{\sqrt{21}}I_{l4,3}^{-}\end{aligned} \tag{24a}$$

and

$$\begin{aligned}R_l(2;e_{5/2})&=R_l(2;g_{3/2})\\ &\equiv R_l(2)\\ &=\frac{1}{\sqrt{3}}I_{l1,0}^{-}-\frac{1}{\sqrt{7}}I_{l2,3}^{-}+\frac{2}{\sqrt{21}}I_{l4,3}^{-}\ .\end{aligned} \tag{24b}$$

On comparing (24) with Eqs. (8b) and (8c) derived in Ref. 21, we find that

$$\begin{aligned}&I_{ll',l_b}^{-}=\sum_{l''}R_{ll''}I_{l''l',l_b},\quad R_l(1)=d_l^{\mu=3}(0)\ ,\\ &R_l(2)=-\sqrt{2}d_l^{\mu=3}(+1)\ .\end{aligned} \tag{25}$$

Here the quantities on the right-hand side of (25) are defined[21] for a spin-unresolved $a_1\rightarrow kt_2$ transition in randomly oriented T_d molecules. Consequently, (21) in the absence of SOI becomes

$$\begin{aligned}&R_l(1-)=R_l(2-)=0\ ,\\ &R_l(1+)=3R_l(1)=3d_l^{\mu=3}(0)\ ,\\ &R_l(2+)=3R_l(2)=-3\sqrt{2}d_l^{\mu=2}(+1)\ .\end{aligned} \tag{26}$$

The matrices (22) now reduce to the following simplified forms:

$$\begin{aligned}d_l^{\tau=1}(0)&=d_l^{\tau=2}(0)\\ &=d_l^{\tau=3}(-1)=d_l^{\tau=3}(+1)=\underline{0}\ ,\\ d_l^{\tau=1}(-1)&=-d_l^{\tau=1}(+1)\\ &=\frac{1}{\sqrt{2}}d_l^{\tau=3}(0)=\frac{1}{3\sqrt{2}}R_l(1+)\underline{1}\\ &=\frac{1}{\sqrt{2}}R_l(1)\underline{1}\ ,\\ d_l^{\tau=2}(-1)&=d_l^{\tau=2}(+1)=-\frac{1}{3\sqrt{2}}R_l(2+)\underline{1}\\ &=-\frac{1}{\sqrt{2}}R_l(2)\underline{1}\ ,\end{aligned} \tag{27}$$

where $\underline{0}$ is a 2×2 null matrix. Because all the nonzero amplitudes (27) are proportional to a unit matrix, they will therefore not give rise to any spin polarization of photoelectrons. Furthermore, all of the transition moments (27) are exactly the same as we found in our previous study[21] of photoionization in a_1 orbital in a T_d molecule without any spin detection.

IV. PHOTOELECTRON ANGULAR DISTRIBUTION

The angular distribution of spin-polarized electrons ejected in photoionization of randomly oriented nonlinear molecules is given by Eq. (I.35). Although the expressions (I.36b)–(I.40b) in terms of the angular momentum transfer for the five parameters present in (I.35) are considerably simpler compared to their counterpart formulas (I.36a)–(I.40a), the actual evaluation of the former is still a tedious process. In order to be able to use (I.36b)–(I.40b), one first needs to know the reduced amplitudes (I.34). In the present example of $a_1 \rightarrow kt_2$ transition in a T_d molecule one has

$$d_{lj,\nu_b}(j_t m_t) = (-i)^l e^{i\sigma_l}(2j+1)\sqrt{2l+1}$$
$$\times \sum_{\tau=1}^{3} \sum_{m=-l}^{l} \sum_{\lambda_r=-1}^{+1} \sum_{\nu=-1/2}^{+1/2} \sum_{mj=-j}^{j} \begin{pmatrix} l & \frac{1}{2} & j \\ -m & -\nu & m_j \end{pmatrix} \begin{pmatrix} 1 & j & j_t \\ \lambda_r & -m_j & m_t \end{pmatrix} b_{lm}^{\tau} d_{l\nu,\nu_b}^{\tau}(\lambda_r) \; . \tag{28}$$

Here we have not written, for brevity, the superscript $p = t_2$, the subscripts $\frac{1}{2}$ and h present in the original expression (I.34). Because $m_t = -j_t, -j_t+1, \ldots, j_t-1, j_t$ and $\nu_b = \pm\frac{1}{2}$, there will therefore be $2(2j_t+1)$ reduced amplitudes (28) for each value of j_t.

Let us consider $l=1$ and 2 in the t_2 continuum orbital, i.e., the photoelectron represented by p and d partial waves only. Then the allowed values of j and j_t are $j=\frac{1}{2},\frac{3}{2}$, $j_t=(\frac{1}{2},\frac{3}{2}),(\frac{1}{2},\frac{3}{2},\frac{5}{2})$ for $l=1$, $j=\frac{3}{2},\frac{5}{2}$, $j_t=(\frac{1}{2},\frac{3}{2},\frac{5}{2}),(\frac{3}{2},\frac{5}{2},\frac{7}{2})$ for $l=2$. The total number of reduced amplitudes (28) is therefore

$$2\left[\sum_{j_t=1/2}^{3/2}(2j_t+1) + \sum_{j_t=1/2}^{5/2}(2j_t+1)\right] = 36$$

and

$$2\left[\sum_{j_t=1/2}^{5/2}(2j_t+1) + \sum_{j_t=3/2}^{7/2}(2j_t+1)\right] = 60$$

for $l=1$ and $l=2$, respectively. In the present example we found that half of these reduced amplitudes in each case exactly vanish. Half of the remaining nonzero amplitudes are an integral multiple of the rest of the half. Therefore the number of independent nonzero amplitudes is 9 for $l=1$ and 15 for $l=2$. These reduced amplitudes can be written in terms of $R_l(i-)$ and $R_l(i+)$ defined in (21), using the expressions (20) for the transition moments $d_{l\nu,\nu_b}^{\tau}(\lambda_r)$ present in (28). One will readily find with the help of the relations (25)–(27) that in the absence of SOI, the nonzero reduced amplitudes become identical to those derived by us earlier[21,27] in spin-unresolved studies of an $a_1 \rightarrow kt_2$ transition in a T_d molecule.

Next we simplify the expressions (I.36b)–(I.40b) using these amplitudes and obtain the following results for five parameters needed to study angular distribution of spin-resolved photoelectrons ejected by ionization in the a_1 orbital in a T_d molecule:

$$\overline{\sigma} = \frac{2K}{27}\sum_{l=1}^{2}\left[|R_l(2-)|^2 + 2|R_l(1-)|^2 + |R_l(1+)|^2 + \tfrac{1}{2}|R_l(2+)|^2\right] , \tag{29}$$

$$\begin{aligned}\overline{\beta} = \frac{2\overline{\sigma}}{135K}\Big[&2|R_1(2+)|^2 + 7|R_1(1+)|^2 - 7|R_1(1-)|^2 - 2|R_1(2-)|^2 \\ &+ 6\{\mathrm{Re}[R_1(2+)R_1^*(1+)] + \mathrm{Re}[R_1(1-)R_1^*(2-)]\} \\ &- \tfrac{5}{7}\big(2|R_2(2+)|^2 + |R_2(1+)|^2 - |R_2(1-)|^2 - 2|R_2(2-)|^2 \\ &\quad + 6\{\mathrm{Re}[R_2(2+)R_2^*(1+)] + \mathrm{Re}[R_2(1-)R_2^*(2-)]\}\big)\Big] ,\end{aligned} \tag{30}$$

$$\overline{\gamma} = \frac{K}{27\overline{\sigma}}\sum_{l=1}^{2}\{|R_l(1-)|^2 + 2\,\mathrm{Re}[R_l(1+)R_l^*(1-)]\} , \tag{31}$$

$$\overline{\delta} = -\frac{2K}{9\overline{\sigma}}\sum_{l=1}^{2}(\tfrac{1}{5}\delta_{1l} - \tfrac{1}{7}\delta_{2l})\{\tfrac{2}{3}|R_l(1-)|^2 - \mathrm{Re}[R_l(2-)R_l^*(1-)] - \tfrac{2}{3}\mathrm{Re}[R_l(1+)R_l^*(1-)] - \mathrm{Re}[R_l(2+)R_l^*(1-)]\} , \tag{32}$$

and

$$\begin{aligned}\overline{\xi} = -\frac{K}{45\overline{\sigma}}\big(&\mathrm{Im}[R_1(2+)R_1^*(1-)] + 4\mathrm{Im}[R_1(1+)R_1^*(1-)] + \mathrm{Im}[R_1^*(1-)R_1(2-)] \\ &- \tfrac{5}{7}\{\mathrm{Im}[R_2(2+)R_2^*(1-)] + \mathrm{Im}[R_2^*(1-)R_2(2-)]\}\big) .\end{aligned} \tag{33}$$

In these expressions and hereafter Re and Im, respectively, mean the real and imaginary parts of the expressions enclosed in the brackets that immediately follow.

On substituting for $R_l(i-)$ and $R_l(i+)$ from (21) in (29)–(33), we find that

$$\bar{\sigma}=\frac{K}{9}\sum_{l=1}^{2}\{2[2|R_l(1;g_{3/2})|^2+|R_l(1;e_{5/2})|^2]+2|R_l(2;g_{3/2})|^2+|R_l(2;e_{5/2})|^2\}\ , \tag{34}$$

$$\begin{aligned}\beta=\frac{4K}{45\sigma}(&\tfrac{7}{2}|R_1(1;g_{3/2})|^2+|R_1(2;g_{3/2})|^2+5\,\mathrm{Re}[R_1(1;g_{3/2})R_1^*(2;g_{3/2})]\\&+7\,\mathrm{Re}[R_1(1;g_{3/2})R_1^*(1;e_{5/2})]+\mathrm{Re}[R_1(1;g_{3/2})R_1^*(2;e_{5/2})]\\&+\mathrm{Re}[R_1(2;g_{3/2})R_1^*(1;e_{5/2})]+2\,\mathrm{Re}[R_1(2;g_{3/2})R_1^*(2;e_{5/2})]+2\,\mathrm{Re}[R_1(1;e_{5/2})R_1^*(2;e_{5/2})]\\&-\tfrac{5}{7}\{\tfrac{1}{2}|R_2(1;g_{3/2})|^2+|R_2(2;g_{3/2})|^2+5\,\mathrm{Re}[R_2(1;g_{3/2})R_2^*(2;g_{3/2})]\\&\quad+\mathrm{Re}[R_2(1;g_{3/2})R_2^*(1;e_{5/2})]+\mathrm{Re}[R_2(1;g_{3/2})R_2^*(2;e_{5/2})]\\&\quad+\mathrm{Re}[R_2(2;g_{3/2})R_2^*(1;e_{5/2})]+2\,\mathrm{Re}[R_2(2;g_{3/2})R_2^*(2;e_{5/2})]+2\,\mathrm{Re}[R_2(1;e_{5/2})R_2^*(2;e_{5/2})]\})\ ,\end{aligned} \tag{35}$$

$$\bar{\gamma}=\frac{K}{27\bar{\sigma}}\sum_{l=1}^{2}\{5|R_l(1;g_{3/2})|^2-|R_l(1;e_{5/2})|^2-4\,\mathrm{Re}[R_l(1;g_{3/2})R_l^*(1;e_{5/2})]\}\ , \tag{36}$$

$$\begin{aligned}\bar{\delta}=\frac{2K}{45\bar{\sigma}}\sum_{l=1}^{2}(\delta_{1l}-\tfrac{5}{7}\delta_{2l})(&\tfrac{2}{3}\{|R_l(1;g_{3/2})|^2-2|R_l(1;e_{5/2})|^2+\mathrm{Re}[R_l(1;g_{3/2})R_l^*(1;e_{5/2})]\}\\&+3\mathrm{Re}\{[R_l(1;g_{3/2})-R_l(1;e_{5/2})]R_l^*(2;g_{3/2})\})\ ,\end{aligned} \tag{37}$$

$$\begin{aligned}\bar{\xi}=-\frac{K}{15\bar{\sigma}}(&4\,\mathrm{Im}[R_1^*(1;g_{3/2})R_1(1;e_{5/2})]-\mathrm{Im}\{[R_1(1;g_{3/2})-R_1(1;e_{5/2})]R_1^*(2;g_{3/2})\}\\&+\tfrac{5}{7}\,\mathrm{Im}\{[R_2(1;g_{3/2})-R_2(1;e_{5/2})]R_2^*(2;g_{3/2})\})\ .\end{aligned} \tag{38}$$

A straightforward application of the relations (24) and (25) show that the five parameters (34)–(38) in the absence of SOI become

$$\bar{\sigma}=\frac{2K}{3}\sum_{l=1}^{2}[|d_l^{\mu=2}(1)|^2+|d_l^{\mu=3}(0)|^2]\ , \tag{39a}$$

$$\begin{aligned}\bar{\beta}=\frac{K}{\bar{\sigma}}(&\tfrac{2}{15}[4|d_1^{\mu=2}(1)|^2+7|d_1^{\mu=2}(0)|^2]-\tfrac{2}{21}[4|d_2^{\mu=2}(1)|^2+|d_2^{\mu=3}(0)|^2]\\&-4\sqrt{2}\{\tfrac{1}{5}\mathrm{Re}[d_1^{\mu=2}(1)d_1^{\mu=3^*}(0)]-\tfrac{1}{7}\mathrm{Re}[d_2^{\mu=2}(1)d_2^{\mu=3^*}(0)]\})\ ,\end{aligned} \tag{39b}$$

and

$$\bar{\gamma}=\bar{\delta}=\bar{\xi}=0\ . \tag{39c}$$

The respective expressions (39a) and (39b) for $\bar{\sigma}$ and $\bar{\beta}$ are exactly the same as derived by us earlier in Eq. (11) in Ref. 21 for photoionization in an a_1 orbital in an unoriented T_d molecule when no spin effects are taken into account. Because the degree of polarization (I.42) of photoelectrons completely depend upon $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\xi}$, the vanishing of these three spin parameters in Eq. (39c) simply means that the ejected electrons have no spin polarization when the SOI in the photoionizing transition $a_1 \rightarrow kt_2$ in a T_d molecule is not included.

In order to write the expressions (29)–(33) in an alternative form, let us define

$$X_l(i)=R_l(i+)/R_l(i-) \tag{40a}$$

and

$$X_l(2,1)=R_l(2+)/R_l(1-)\ , \tag{40b}$$

where $R_l(i+)$ and $R_l(i-)$ have already been introduced through Eqs. (21). The five parameters therefore become

$$\bar{\sigma}=\frac{K}{27}\sum_{l=1}^{2}\{2|R_l(1-)|^2[2+|X_l(1)|^2]+|R_l(2-)|^2[2+|X_l(2)|^2]\}\ , \tag{41a}$$

$$\begin{aligned}\bar{\beta}=-\frac{2K}{135\bar{\sigma}}[&7|R_1(1-)|^2[1-|X_1(1)|^2]+2|R_1(2-)|^2[1-|X_1(2)|^2]-6\,\mathrm{Re}\{R_1(1-)R_1^*(2-)[1+X_1(1)X_1^*(2)]\}\\&-\tfrac{5}{7}(|R_2(1-)|^2[1-|X_2(1)|^2]+2|R_2(2-)|^2[1-|X_2(2)|^2]\\&-6\,\mathrm{Re}\{R_2(1-)R_2^*(2-)[1+X_2(1)X_2^*(2)]\})]\ ,\end{aligned} \tag{41b}$$

$$\bar{\gamma}=\frac{K}{27\bar{\sigma}}\sum_{l=1}^{2}|R_l(1-)|^2[1+X_l(1)+X_l^*(1)]\ , \tag{41c}$$

$$\bar{\delta}=\frac{2K}{135\bar{\sigma}}\sum_{l=1}^{2}(\delta_{1l}-\tfrac{5}{7}\delta_{2l})(|R_l(1-)|^2[X_l(1)+X_l^*(1)-2]+3\,\mathrm{Re}\{R_l(1-)R_l^*(2-)[1+X_l^*(2)]\})\ , \tag{41d}$$

$$\begin{aligned}\bar{\xi}=-\frac{K}{45\bar{\sigma}}[&|R_1(1-)|^2(4\,\mathrm{Im}X_1(1)+\mathrm{Im}\{X_1(2,1)[1+X_1(2)]/X_1(2)\})\\&-\tfrac{5}{7}|R_2(1-)|^2\mathrm{Im}\{X_2(2,1)[1+X_2(2)]/X_2(2)\}]\ .\end{aligned} \tag{41e}$$

V. DEGREE OF SPIN POLARIZATION

A. Approximations and their validity

In order to proceed further, both the magnitude as well as phase of the $E1$ ionization integrals $R_l(i;q)$, which are defined in Eqs. (19) and are present in the five expressions (34)–(38), 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 perform any dynamical calculations. These ionization integrals are, instead, extracted from whatever experimental information we have on photoionization in the a_1 orbital of an unoriented T_d molecule.

It is obvious that for each lth partial wave used to represent the photoelectron, one requires four R's, i.e., $R_l(1;e_{5/2})$, $R_l(1;g_{3/2})$, $R_l(2;e_{5/2})$, and $R_l(2;g_{3/2})$. Hitherto, on the other hand, the only measurements available are on $\bar{\sigma}$ and $\bar{\beta}$ for angular distribution of photoelectrons produced by a spin-unresolved bound-free transition in those targets whose point symmetry group is T_d. In order to determine $R_l(i;q)$ from the available experimental data, it thus becomes necessary that their number be reduced. It can readily be done by using some of those assumptions which were introduced in studying the photoionization in a T_d molecule with both random[21,27,28] as well as fixed[29] orientation in space in the absence of SOI.

In particular, we consider only the lowest[20] $l_b=0$ term in the single-center expansion (2) for the bound a_1 orbital in a T_d molecule. In this approximation, the dipole integrals $I^{q-}_{l2,3}$ and $I^{q-}_{l4,3}$, which are associated with the second[20] (i.e., $l_b=3$) term in the expansion (2), will not occur. The two Eqs. (19) therefore give

$$R_l(1;q)=R_l(2;q)=\frac{1}{\sqrt{3}}I^{q-}_{l1,0}\equiv R_l(q)\ , \tag{42}$$

where the radial dipole integral I^{q-}_{ll',l_b} is defined in (17). On the application of the approximation (42), the expressions (34)–(38) take the following simplified forms:

$$\bar{\sigma}=\frac{K}{3}\sum_{l=1}^{2}(2|R_l(g_{3/2})|^2+|R_l(e_{5/2})|^2)\ , \tag{43}$$

$$\begin{aligned}\bar{\beta}=\frac{2K}{45\bar{\sigma}}(&19|R_1(g_{3/2})|^2+4|R_1(e_{5/2})|^2+22\,\mathrm{Re}[R_1(g_{3/2})R_1^*(e_{5/2})]\\&-\tfrac{5}{7}\{13|R_2(g_{3/2})|^2+4|R_2(e_{5/2})|^2+10\,\mathrm{Re}[R_2(g_{3/2})R_2^*(e_{5/2})]\})\ ,\end{aligned} \tag{44}$$

$$\bar{\gamma}=\frac{K}{27\bar{\sigma}}\sum_{l=1}^{2}\{5|R_l(g_{3/2})|^2-|R_l(e_{5/2})|^2-4\,\mathrm{Re}[R_l(g_{3/2})R_l^*(e_{5/2})]\}\ , \tag{45}$$

$$\bar{\delta}=\frac{2K}{135\bar{\sigma}}\sum_{l=1}^{2}(\delta_{1l}-\tfrac{5}{7}\delta_{2l})\{11|R_l(g_{3/2})|^2-4|R_l(e_{5/2})|^2-7\,\mathrm{Re}[R_l(g_{3/2})R_l^*(e_{5/2})]\}\ , \tag{46}$$

$$\bar{\xi}=-\frac{K}{3\bar{\sigma}}\{\mathrm{Im}[R_1^*(g_{3/2})R_1(e_{5/2})]-\tfrac{1}{7}\mathrm{Im}[R_2^*(g_{3/2})R_2(e_{5/2})]\}\ . \tag{47}$$

The expressions (21), (40), and (41), on the other hand, become

$$R_l(1-)=R_l(2-)=R_l(g_{3/2})-R_l(e_{5/2})\equiv R_l(-)\ , \tag{48a}$$

$$R_l(1+)=R_l(2+)=2R_l(g_{3/2})+R_l(e_{5/2})\equiv R_l(+)\ , \tag{48b}$$

$$X_l(1)=X_l(2)=X_l(2,1)=R_l(+)/R_l(-)\equiv X_l\ , \tag{48c}$$

$$\bar{\sigma}=\frac{K}{9}\sum_{l=1}^{2}|R_l(-)|^2(2+|X_l|^2)\ , \tag{49a}$$

$$\bar{\beta}=-\frac{2K}{45\bar{\sigma}}[|R_1(-)|^2(1-5|X_1|^2)+\tfrac{5}{7}|R_2(-)|^2(1+3|X_2|^2)]\ , \tag{49b}$$

$$\bar{\gamma}=\frac{K}{27\bar{\sigma}}\sum_{l=1}^{2}|R_l(-)|^2(1+X_l+X_l^*)\ , \tag{49c}$$

$$\bar{\delta}=\frac{K}{27\bar{\sigma}}\sum_{l=1}^{2}(\delta_{1l}-\tfrac{5}{7}\delta_{2l})|R_l(-)|^2(\tfrac{2}{5}+X_l+X_l^*)\ , \tag{49d}$$

$$\bar{\xi}=-\frac{K}{9\bar{\sigma}}(|R_1(-)|^2\mathrm{Im}X_1-\tfrac{1}{7}|R_2(-)|^2\mathrm{Im}X_2)\ . \tag{49e}$$

Let us introduce one more approximation by representing the photoelectron by a single p ($l=1$) partial wave. Obviously, one cannot expect that such simple considerations will adequately describe the angle- and spin-resolved photoionization in the a_1 orbital of an unoriented T_d molecule. However, the motivation for the present study is, in addition to other reasons, to demonstrate as to how the multichannel theory developed in the preceding paper[9] for ASPRES in nonlinear molecules can be applied to a real situation, the use of the group-theoretical methods simplifies an otherwise extremely complex problem to maximum possible extent, and to show that in general spin-polarized electrons can be expected in photoionization of even randomly oriented nonlinear targets by linearly and circularly, as well as unpolarized, light when the SOI is present only 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 molecules, our calculation serves 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 molecular orbitals more satisfactorily. Needless to say, it will prohibitively be difficult to perform such *ab initio* calculations for complicated nonlinear molecules whose point symmetry group is T_d.

Equations (43)–(47) now become

$$\bar{\sigma}=\frac{K}{3}[2|R_1(g_{3/2})|^2+|R_1(e_{5/2})|^2]\ , \tag{50a}$$

$$\bar{\beta}=\frac{2K}{45\bar{\sigma}}\{19|R_1(g_{3/2})|^2+4|R_1(e_{5/2})|^2+22\,\mathrm{Re}[R_1(g_{3/2})R_1^*(e_{5/2})]\}\ , \tag{50b}$$

$$\bar{\gamma}=\frac{K}{27\bar{\sigma}}\{5|R_1(g_{3/2})|^2-|R_1(e_{5/2})|^2-4\,\mathrm{Re}[R_1(g_{3/2})R_1^*(e_{5/2})]\}\ , \tag{50c}$$

$$\bar{\delta}=\frac{2K}{135\bar{\sigma}}\{11|R_1(g_{3/2})|^2-4|R_1(e_{5/2})|^2-7\,\mathrm{Re}[R_1(g_{3/2})R_1^*(e_{5/2})]\}\ , \tag{50d}$$

$$\bar{\xi}=-\frac{K}{3\bar{\sigma}}\mathrm{Im}[R_1^*(g_{3/2})R_1(e_{5/2})]\ . \tag{50e}$$

Equations (50a) and (50b) show that, when $R_1(g_{3/2})=R_1(e_{5/2})$ in the absence of SOI, $\bar{\beta}=2$. This result has already been shown by us[21,27] for the $a_1\rightarrow kt_2$ transition in a T_d molecule if the ejected electron without any spin selection is represented by a p wave only. The same value of $\bar{\beta}$ is obtained[8] when an s shell in an atomic target is photoionized in the absence of SOI. Equation (50a) further shows that for the integrated partial cross section to be nonzero at the Cooper minimum,[16] it is necessary that $R_1(e_{5/2})$ and $R_1(g_{3/2})$ must vanish at different photon energies. Therefore at a Cooper minimum corresponding to $R_1(e_{5/2})=0$, we have

$$\bar{\beta}=\tfrac{19}{15},\quad \bar{\gamma}=\tfrac{5}{18},\quad \bar{\delta}=\tfrac{11}{45},\quad \bar{\xi}=0\ . \tag{51a}$$

On the other hand, if $R_1(g_{3/2})=0$, then

$$\bar{\beta}=\tfrac{8}{15},\quad \bar{\gamma}=-\tfrac{1}{9},\quad \bar{\delta}=-\tfrac{8}{45},\quad \bar{\xi}=0\ . \tag{52a}$$

It should therefore be possible to determine experimentally the photon wavelengths when either of the two transition moments $R_1(e_{5/2})$ or $R_1(g_{3/2})$ becomes zero. (In the case of photoionization in an atomic target, $\bar{\beta}$ is instead 1 and 0 when the dipole matrix elements for the transitions $ns\rightarrow kp_{1/2}$ and $ns\rightarrow kp_{3/2}$ vanish, respectively.[23,30])

It has already been shown in the preceding paper[9] that the degree of spin polarization of the photoelectrons is proportional to $\bar{\xi}$ when the incident light is either linearly polarized [Eqs. (I.44) and (I.45)] or unpolarized [Eqs. (I.50) and (I.51)]. Equation (I.48) further shows that $P(m_r=\pm1,\ \hat{\mathbf{u}}'_{\mathrm{trans},\perp};\ \mathbf{k}')$ for electrons ejected even by a circularly polarized photon beam is also proportional to $\bar{\xi}$. According to Eqs. (51a) and (52a), there will not be any spin selection of photoelectrons in the region of Cooper minimum in these three cases.

It is, furthermore, obvious from Eqs. (I.47) and (I.49) that the degrees $P(m_r=\pm1,\ \hat{\mathbf{u}}'_{\mathrm{long}};\ \mathbf{k}')$ and $P(m_r=\pm1,\ \hat{\mathbf{u}}'_{\mathrm{trans}\|};\ \mathbf{k}')$ of spin polarization of electrons ejected by circularly polarized light are respectively proportional to $\bar{\delta}-\bar{\gamma}$ and $2\bar{\gamma}+\bar{\delta}$. Equations (51a) and (52a), on the other hand, give

$$\bar{\delta}-\bar{\gamma}=-\tfrac{1}{30},\quad 2\bar{\gamma}+\bar{\delta}=\tfrac{4}{5} \tag{51b}$$

and

$$\bar{\delta}-\bar{\gamma}=-\tfrac{1}{15},\quad 2\bar{\gamma}+\bar{\delta}=-\tfrac{2}{5} \tag{52b}$$

when $R_1(e_{5/2})=0$ and $R_1(g_{3/2})=0$, respectively. One therefore obtains from Eqs. (I.47), (I.49), and (51b) that at the magic angle ($\theta'=54.74°$)

$$P(m_r=\pm1,\hat{\mathbf{u}}'_{\text{long}};\mathbf{k}')=-m_r\frac{1}{30\sqrt{3}}\ , \tag{51c}$$

$$P(m_r=\pm1,\hat{\mathbf{u}}'_{\text{trans},\parallel};\mathbf{k}')=m_r\tfrac{2}{5}\sqrt{2/3} \tag{51d}$$

when $R_1(e_{5/2})=0$ for circularly polarized light in the region of Cooper[16] minimum. On combining (I.47) and (I.49) with the result (52b) for Cooper minimum with $R_1(g_{3/2})=0$, one further has

$$P(m_r=\pm1,\hat{\mathbf{u}}'_{\text{long}};\mathbf{k}')=-m_r\frac{1}{15\sqrt{3}}\ , \tag{52c}$$

$$P(m_r=\pm1,\hat{\mathbf{u}}'_{\text{trans},\parallel};\mathbf{k}')=-m_r\tfrac{1}{5}\sqrt{2/3} \tag{52d}$$

for photoionization by circularly polarized light at the magic angle again.

The simplified form of Eqs. (49), obtained by representing the departing electron by a p ($l=1$) wave only, is

$$\bar{\sigma}=\frac{K}{9}|R_1(-)|^2(2+|X_1|^2)\ , \tag{53a}$$

$$\bar{\beta}=-\frac{2}{5}\,\frac{1-5|X_1|^2}{2+|X_1|^2}\ , \tag{53b}$$

$$\bar{\gamma}=\frac{1}{3}\,\frac{1+2|X_1|\cos\Delta_1}{2+|X_1|^2}\ , \tag{53c}$$

$$\bar{\delta}=\frac{2}{3}\,\frac{\frac{1}{5}+|X_1|\cos\Delta_1}{2+|X_1|^2}\ , \tag{53d}$$

$$\bar{\xi}=-\frac{|X_1|\sin\Delta_1}{2+|X_1|^2}\ , \tag{53e}$$

$$\bar{\delta}-\bar{\gamma}=-\frac{1}{5(2+|X_1|^2)}\ , \tag{53f}$$

$$2\bar{\gamma}+\bar{\delta}=2\frac{\frac{2}{5}+|X_1|\cos\Delta_1}{2+|X_1|^2}\ , \tag{53g}$$

with

$$X_1=|X_1|e^{i\Delta_1}\ . \tag{53h}$$

Equations (53f) and (53g) have here been obtained by combining (53c) and (53d). The relationship (53f) obviously means that $\gamma>\delta$ always.

We know from (I.43) that the degree of spin polarization of the total photocurrent is proportional to $\bar{\gamma}$ for circularly polarized incident light. On comparing our Eq. (53c) for $\bar{\gamma}$ with Eq. (5) given by Fano,[22] one can say that the parameter X_l defined in Eqs. (40) in this paper is a multichannel generalization in the context of molecular photoionization of x introduced by Fano[22] in his Eq. (6) for describing the spin-polarization of atomic photoelectrons ejected by circularly polarized light. (In Fano's case,[22] x is real.)

The two quantities, defined in (53h), now needed are the magnitude $|X_1|$ and the phase Δ_1 of X_1. These can be obtained from a knowledge of any of the two parameters $\bar{\beta}$, $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\xi}$. The inverse of (53b) directly gives the magnitude

$$|X_1|^2=2\frac{\frac{1}{5}+\bar{\beta}}{2-\bar{\beta}}\ . \tag{54}$$

It is well known that the asymmetry in the angular distribution of electrons ejected in photoionization of unoriented molecules is always in the range $-1\le\bar{\beta}\le2$. Equation (54) will give $|X_1|^2$ to be negative if $-1<\bar{\beta}<-\frac{1}{5}$. For all the T_d molecules[17,18,31–34] whose angle-resolved photoelectron spectra (ARPES) of the a_1^2 orbital has been taken so far, $\bar{\beta}$ is always greater than $-\frac{1}{5}$. Equation (54) can therefore be used to extract the magnitude of X_1 from the experimental data on $\bar{\beta}$ in all such cases.

In order to determine the phase Δ_1, knowledge of any one of the three spin-parameters $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\xi}$ is required. It is obvious from Eqs. (53) that only $\bar{\xi}$ is proportional to $\sin\Delta_1$, whereas the rest involve the cosine of Δ_1. Hence, a measurement of $\bar{\xi}$ will give us information on both sign and magnitude of the phase angle Δ_1. According to Eqs. (I.44) and (I.50), $\bar{\xi}$ can be obtained by measuring the degree of spin polarization of electrons ejected by either linearly polarized or unpolarized light, respectively. If circularly polarized light is used, on the other hand, one then needs to measure $P(m_r=\pm1,\ \hat{\mathbf{u}}'_{\text{trans},\perp};\ \mathbf{k}')$ to find $\bar{\xi}$ from Eq. (I.48).

B. Results

The results presented in the following are based on Eqs. (53e)–(53g) and (54). The three examples considered in this paper are photoionization in $4a_1^2$, $6a_1^2$, and $7a_1^2$ orbitals of CF_4, CCl_4, and $SiCl_4$, respectively. The only measurement available to us in all these cases, in addition to the integrated cross section $\bar{\sigma}$, is that of $\bar{\beta}$ as a function of photon wave length. Equations (54) and (53f), neither of which involves the phase Δ_1, should describe the energy-dependent behavior of the magnitude $|X_1|$ and of $\bar{\delta}-\bar{\gamma}$, respectively. The later of these two, according to Eq. (I.47), determines the degree $P(m_r=\pm1,\ \hat{\mathbf{u}}'_{\text{long}};\ \mathbf{k}')$ of spin polarization of photoelectrons produced by circularly polarized light. Application of Eqs. (53e) and (53g) requires, on the other hand, knowledge of the angle Δ_1 which has here been treated as a parameter. $2\bar{\gamma}+\bar{\delta}$ in (53g) is needed in calculating $P(m_r=\pm1,\ \hat{\mathbf{u}}'_{\text{trans},\parallel};\ \mathbf{k}')$ from Eq. (I.49); whereas $\bar{\xi}$, given by (53e), is required in (I.44), (I.48), and (I.50).

Furthermore, because $\cos(\pi-\Delta_1)=\cos(\pi+\Delta_1)$, $2\bar{\gamma}+\bar{\delta}$ is thus symmetric about $\Delta_1=\pi$. It is therefore sufficient to consider (53g) for $0\le\Delta_1\le\pi$ only. $\bar{\xi}$ in (53e), on the other hand, is symmetric about $\Delta_1=\pi/2$ because of the property $\sin(\pi/2-\Delta_1)=\sin(\pi/2+\Delta_1)$. One therefore needs to consider in this case only $0\le\Delta_1\le\pi/2$. However, if $\Delta_1>\pi$, one can then obtain $\bar{\xi}$ from its values for $\Delta_1<\pi$ using the relation $\sin(\pi-\Delta_1)=-\sin(\pi+\Delta_1)$. [It is, of course, obvious from (53e) that $\bar{\xi}$ always vanishes whenever $\Delta_1=n\pi$, $n=0$–2.] The following calculations of $\bar{\xi}$ and of $2\bar{\gamma}+\bar{\delta}$ have therefore been done only for $\Delta_1=(\pi/6,\pi/3,\pi/2)$ and ($n\pi/4, n=0$–4), respectively.

1. Photoionization in $4a_1^2$ orbital of CF_4

Carlson *et al.*[32] have extracted both $\bar{\sigma}$ and $\bar{\beta}$ from their ARPES of $4a_1^2$ orbital in gaseous, unoriented CF_4 for incident photon energies from 28 to 70 eV. Novak *et al.*[33] 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 $-\frac{1}{5}$, we have therefore used Eqs. (53) and (54) for studying angle- and spin-resolved photoionizing transitions $4a_1^2 \to 4a_1^1(e_{1/2})kt_2(e_{5/2},g_{3/2})$ in CF_4.

Our results for ξ and $\bar{\delta}-\bar{\gamma}$ calculated from Eqs. (53e) and (53f), respectively, along with $|X_1|$ obtained from (54), and the measured[32] values of $\bar{\beta}$ are shown in Fig. 1(a) as a function of energy (E_r) of the incident radiation.

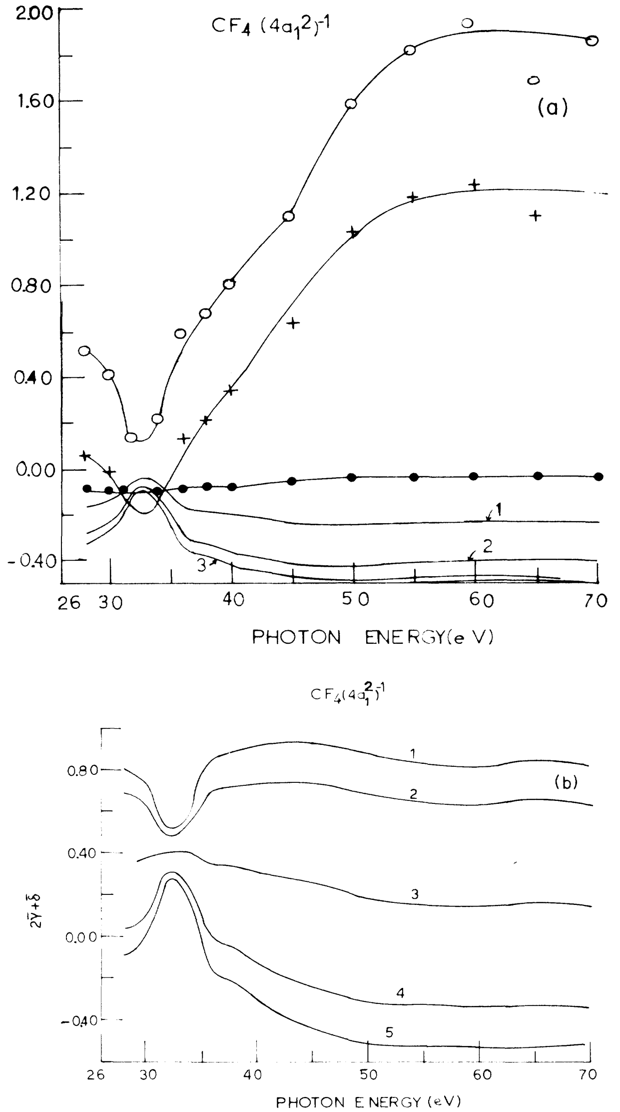

FIG. 1. (a) Variation of $\bar{\beta}$, $|X_1|$, $\bar{\delta}-\bar{\gamma}$, and of ξ with photon energy for ionization in $4a_1^2$ orbital of unoriented CF_4. Experimental values of $\bar{\beta}$ measured by Carlson *et al.* (Ref. 32), +; $|X_1|$ calculated from Eq. (54), ○; $\bar{\delta}-\bar{\gamma}$ calculated from Eq. (53f), ●; 1.40ξ calculated from Eq. (53e) for $\Delta_1=\pi/6$ (curve 1), $\pi/3$ (curve 2), and $\pi/2$ (curve 3). (ξ is zero for $\Delta_1=0,\pi$.) (b) Variation of $2\bar{\gamma}+\bar{\delta}$ with photon energy for ionization in the $4a_1^2$ orbital of freely rotating CF_4 calculated from Eq. (53g) using $|X_1|$ shown in (a). $\Delta_1=0$, curve 1; $\Delta_1=\pi/4$, curve 2; $\Delta_1=\pi/2$, curve 3; $\Delta_1=3\pi/4$, curve 4; $\Delta_1=\pi$, curve 5.

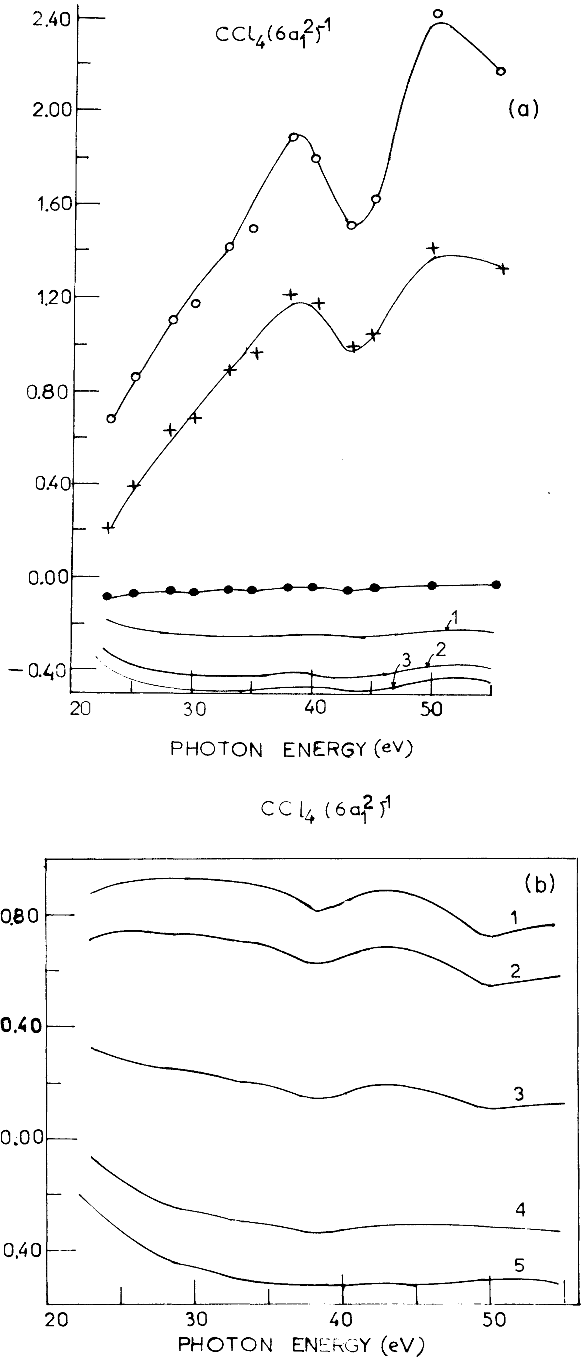

FIG. 2. (a) Same as Fig. 1(a) but for photoionization in the $6a_1^2$ orbital of randomly oriented CCl_4. The values of $\bar{\beta}$ shown are those measured by Carlson *et al.* (Ref. 17). (b) Same as Fig. 1(b) but for photoionization in the $6a_1^2$ orbital of freely rotating CCl_4. The values of $|X_1|$ used are those shown in (a).

Figure 1(b), on the other hand, contains $2\bar{\gamma}+\bar{\delta}$ computed using Eq. (53g) as a function of the energy of the ionizing photon. While $\bar{\delta}-\bar{\gamma}$ does not seem to change much with E_r on the scale of Fig. 1(a), the behavior of $|X_1|$ with the photon energy is very similar to that of $\bar{\beta}$. Both $\bar{\xi}$ and $2\bar{\gamma}+\bar{\delta}$ vary most with the energy of ionizing radiation for E_r up to about 40 eV for all values of the phase angle Δ_1 $[=(\pi/6,\pi/3,\pi/2)$ and $(n\pi/4, n=0-4)$, respectively] considered in this paper. The interesting thing here is that while $\bar{\xi}$ in Fig. 1(a) increases and $2\bar{\gamma}+\bar{\delta}$ in Fig. 1(b) either decreases or increases following rapid fall in $\bar{\beta}$, where it becomes negative for E_r between about 30–35 eV, $\bar{\delta}-\bar{\gamma}$ remains unaffected even in this part of the ionization region.

Furthermore, there is a significant change in $\bar{\xi}$ as well as in $2\bar{\gamma}+\bar{\delta}$ with the phase angle Δ_1 over the whole range of photon energies shown in the two parts of Fig. 1. [$\bar{\delta}-\bar{\gamma}$ is not affected by a change in the phase because Eq. (53f) is independent of Δ_1.] Particularly, in the case of $2\bar{\gamma}+\bar{\delta}$, a valley between $E_r=30$–35 eV for $\Delta_1<\pi/2$ begins to grow in the shape of a large hump as Δ_1 increases from $\pi/2$. Such behavior of both $\bar{\xi}$ and $2\bar{\gamma}+\bar{\delta}$ suggests that both of them are very sensitive to a change in the phase Δ_1.

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

The values of $\bar{\beta}$ used in Eq. (54) in this case are those measured by Carlson *et al.*[17] for spin-unresolved photoionization in $6a_1^2$ orbital of randomly oriented CCl_4. The energies of the incident radiation considered are from 23 to 55 eV. The observed[17] $\bar{\beta}$, corresponding $|X_1|$, and also $\bar{\delta}-\bar{\gamma}$ as well as $\bar{\xi}$ calculated from Eqs. (53f) and (53e), respectively, are shown in Fig. 2(a) as a function of the photon energy. The $2\bar{\gamma}+\bar{\delta}$ obtained from (53g) for five different values of Δ_1 is plotted in Fig. 2(b).

Here again we see that, similar to what we found in Fig. 1(a) for photoionization in $4a_1^2$ orbital of CF_4, the behavior of the magnitude of $|X_1|$ with E_r in Fig. 2(a) is about the same as that of $\bar{\beta}$ and also $\bar{\delta}-\bar{\gamma}$ does not vary much on the scale of this figure. Further, both $\bar{\xi}$ in Fig. 2(a) and $2\bar{\gamma}+\bar{\delta}$ in Fig. 2(b) have very strong dependence on the phase Δ_1. However, unlike in the previous case, neither of the two has variations similar to those of $\bar{\beta}$ in any part of the ionization region considered in Figs. 2. Also, both in Figs. 1(a) and 2(a), $|\bar{\delta}-\bar{\gamma}|$ is minimum among the three quantities ($|\bar{\xi}|$, $|\bar{\delta}-\bar{\gamma}|$, and $|2\bar{\gamma}+\bar{\delta}|$) at almost all the energies of the incident radiation considered in the two respective experiments of Carlson *et al.*[32,17]

The present analysis further shows that the cross-section minimum[16] in the CCl_4 $(6a_1^2)^{-1}$ spectrum observed by Carlson *et al.*[17] is due probably to a vanishing contribution of the transition $6a_1^2 \rightarrow 6a_1^1\,(e_{1/2})kt_2(e_{5/2})$ to ionization by ~45-eV photons. Because the measured[17] values of $\bar{\beta}$ in the range $E_r=43$–50 eV, where $\bar{\sigma}$ becomes minimum, and the correspondingly calculated values of $\bar{\delta}-\bar{\gamma}$ and of $2\bar{\gamma}+\bar{\delta}$ (for $\Delta_1=0$) shown in Figs. 2(a) and 2(b), respectively, are almost in agreement with those given in Eqs. (51a) and (51b). One can therefore say that for ionization in $6a_1^2$ orbital of unoriented CCl_4 by photons of energy between about 43–50 eV, $R_1(e_{5/2})$ is almost zero, $X_1\simeq 2$ (with $\Delta_1\simeq 0$), and the photocurrent produced by linearly polarized or unpolarized light will probably have no spin polarization. On the other hand, the degree of spin polarization of electrons ejected at the magic angle by circularly polarized light in the region of Cooper minimum is given by (51c) and (51d).

3. *Photoionization in $7a_1^2$ orbitals of $SiCl_4$*

Carlson *et al.*[18] have taken ARPES of $7a_1^2$ orbital in freely rotating $SiCl_4$ molecules for photon energies from 19 to 80 eV. Because $\bar{\beta}$ in this case is always greater than $-\frac{1}{5}$, the measurements of Carlson *et al.*[18] have therefore

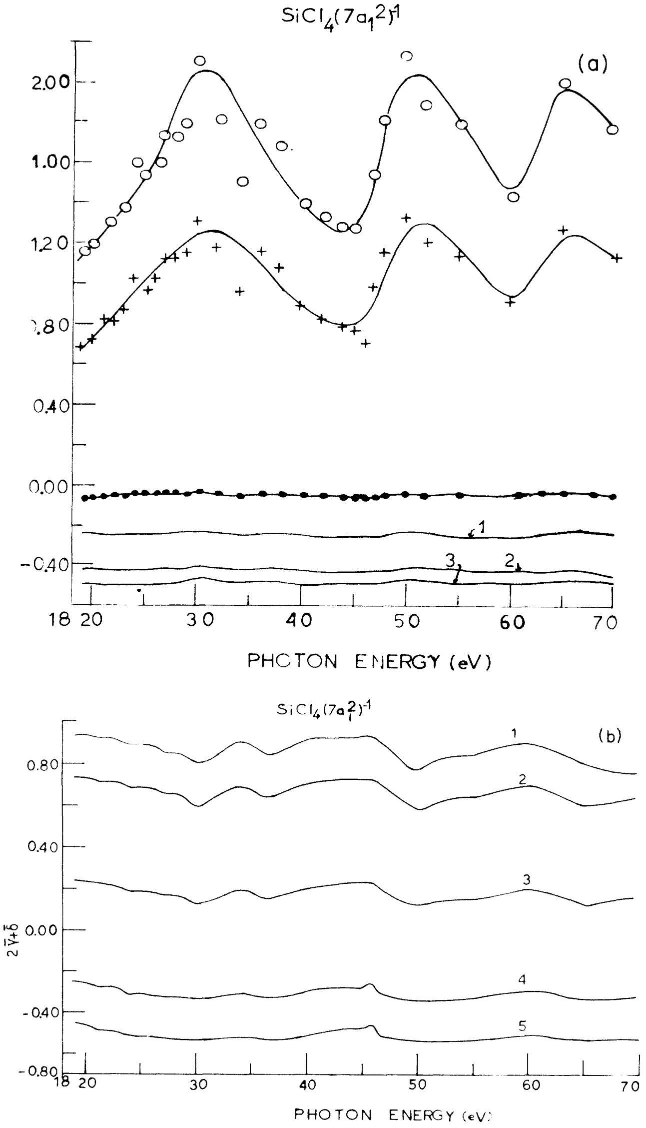

FIG. 3. (a) Same Fig. 1(a) but for photoionization in the $7a_1^2$ orbital of unoriented $SiCl_4$. $\bar{\beta}$ measured by Carlson *et al.* (Ref. 18) has been used in this figure. (b) Same as Fig. 1(b) but for photoionization in the $7a_1^2$ orbital of randomly oriented $SiCl_4$. The values of $|X_1|$ used are taken from (a).

been used here to study spin-resolved photoionization in $7a_1^2$ orbital of unoriented $SiCl_4$.

The values of $|X_1|$ calculated from Eq. (54) and those of $\bar{\xi}$ and of $\bar{\delta}-\bar{\gamma}$ obtained from (53e) and (53f), respectively, are shown in Fig. 3(a) as a function of E_r. Figure 3(b) shows $2\bar{\gamma}+\bar{\delta}$ calculated using Eq. (53g). Although $|X_1|$ again in Fig. 3(a) varies as $\bar{\beta}$ with the energy of the incident radiation, the other three quantities $\bar{\delta}-\bar{\gamma}$, $\bar{\xi}$, and $2\bar{\gamma}+\bar{\delta}$ have small changes with respect to E_r on the scale used in the two parts of Fig. 3. However, both $\bar{\xi}$ and $2\bar{\gamma}+\bar{\delta}$ again have a very strong dependence on Δ_1, and $|\bar{\delta}-\bar{\gamma}|$ is always the minimum at all photon energies considered in these two figures.

Carlson *et al.*[18] have reported a Cooper minimum[16] between $E_r=38-45$ eV in the $(7a_1^2)^{-1}$ spectrum of unoriented $SiCl_4$. On analyzing this data, one finds that the observed $\bar{\beta}$, the corresponding $\bar{\delta}-\bar{\gamma}$ and $2\bar{\gamma}+\bar{\delta}$ (for $\Delta_1=\pi$) shown in Fig. 3 between 38–45 eV are in reasonable agreement with those given in Eqs. (52a) and (52b). Therefore the Cooper minimum[16] in this part of the spectrum is due probably to a vanishing contribution of the ionization integral $R_1(g_{3/2})$ associated with the spin-resolved transition $7a_1^2 \rightarrow 7a_1^1(a_{1/2})kt_2(g_{3/2})$ in $SiCl_4$. Here $X_1 \simeq -1$ (with $\Delta_1 \simeq \pi$) and the degree of spin-polarization of photoelectrons ejected at the magic angle is given by Eqs. (52c) and (52d).

VI. CONCLUSION

In this paper we have applied the theory for ASPRES of nonlinear molecules, developed in the preceding article,[9] to study $a_1 \rightarrow kt_2$ photoionizing transition in randomly oriented T_d molecules. The spin polarization of ejected electrons in this case is due directly to the SOI in the continuum t_2 orbital of the molecular target. After showing that on the inclusion of SOI with spin $s=\frac{1}{2}$ the A_1 and T_2 single-evaluated IR's should, respectively, be associated with the $E_{1/2}$ and $(E_{5/2},G_{3/2})$ IR's of the extended T_d group, the wave functions for the bound and continuum spin orbitals involved in the photoionizing process are written in terms of the basis functions of appropriate double-valued representations. These orbitals are used to obtain expressions for the ionization amplitudes, in the $E1$ length approximation. The amplitudes have been shown to reduce, in the absence of SOI, to those derived by us[21] for spin-unresolved $a_1 \rightarrow kt_2$ transition in a T_d molecule.

The explicit expressions for the five parameters (integrated partial cross section $\bar{\sigma}$, angular asymmetry $\bar{\beta}$, and the three spin parameters $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\xi}$), needed to describe the angular distribution of spin-polarized photoelectrons, are obtained using the angular momentum transfer formalism given in the companion paper.[9] In the absence of SOI, the expressions for reduced amplitudes, $\bar{\sigma}$ and $\bar{\beta}$ become identical to those derived earlier[21,27] for spin-unresolved photoionization; whereas $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\xi}$ vanish identically. The five formulas for $\bar{\sigma}$, $\bar{\beta}$, $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\xi}$ have been written in yet another form by introducing a complex parameter X_l, which is probably a multichannel molecular analog for the lth partial wave of the real variable x used by Fano[22] in his classic paper on spin polarization of total photocurrent produced by interaction of circularly polarized light with Cs atom.

This theory is then applied to photoionization in $4a_1^2$, $6a_1^2$, and $7a_1^2$ orbitals of CF_4, CCl_4, and $SiCl_4$ respectively. The three quantities needed[9] to calculate the degree of spin polarization of electrons ejected by ionization in an unoriented target by unpolarized or linearly or circularly polarized light are $\bar{\xi}$, $\bar{\delta}-\bar{\gamma}$, and $2\bar{\gamma}+\bar{\delta}$. The simple qualitative predictions for each of these are made on the assumptions that only the first $l_b=0$ term is taken into account in the $e_{1/2}$ orbital of the bound electron, whereas the photoelectron in either of its two continuum channels $e_{5/2}$ and $g_{3/2}$ is represented by a p $(l=1)$ partial wave only. These approximations also help in finding the values of $\bar{\beta}$, $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\xi}$ for the two cases when contribution to photoionization of one of the two transitions $a_1^2 \rightarrow a_1^1\ (e_{1/2})kt_2(e_{5/2})$ and $a_1^2 \rightarrow a_1^1\ (a_{1/2})kt_2(g_{3/2})$ vanishes. Either of these situations will give rise to a Cooper minimum[16] in photoionization in a T_d molecule.

It is also shown that while the magnitude $|X_1|$ of X_1 (i.e., X_l for $l=1$) can be extracted from the data on $\bar{\beta}$; knowledge of $\bar{\xi}$, on the other hand, is essential to determine both the sign and the magnitude of the phase Δ_1 of X_1. Although, both $\bar{\xi}$ and $2\bar{\gamma}+\bar{\delta}$ depend upon Δ_1, $\bar{\delta}-\bar{\gamma}$ is independent of this angle. In our calculations for the three examples considered in this paper, we use $\bar{\beta}$ as a function of the energy of the ionizing radiation and treat Δ_1 as a parameter. The results presented here therefore describe the energy-dependent behavior of $|X_1|$ and of $\bar{\delta}-\bar{\gamma}$. Both $\bar{\xi}$ and $2\bar{\gamma}+\bar{\delta}$, on the other hand, are found to have very strong dependence on Δ_1, which in turn depends upon the phases of the dipole matrix elements, and hence is influenced by the SOI in the continuum part of the molecular spectra.

This study has further revealed that the Cooper minima observed in $CCl_4(6a_1^2)^{-1}$ and $SiCl_4(7a_1^2)^{-1}$ spectra[17,18] are probably due, respectively, to the vanishing values of the integrals $R_1(e_{5/2})$ and $R_1(g_{3/2})$, which represent the contributions to the photoionization process of the transitions $6a_1^2 \rightarrow 6a_1^1\ (e_{1/2})kt_2(e_{5/2})$ and $7a_1^2 \rightarrow 7a_1^1\ (e_{1/2})kt_2(g_{3/2})$. We have thus been able to predict the spin parameters $\bar{\gamma}$, $\bar{\delta}$, and $\bar{\xi}$, and both the magnitude as well as the phase of X_1 in the region of the nonzero cross-section minima observed in the two respective spectra.

It is, however, possible that in order to properly take into account the energy-dependent effects and the anisotropic final-state interaction, one needs to perform dynamical calculations including both many-electron forces, the values of $l_b>0$ in the single-center expansion of the $e_{1/2}$ orbital, and represent the photoelectron by partial waves higher than p. But such studies for complex nonlinear targets like those belonging to a T_d point group will be prohibitively arduous.

This article, along with its companion paper,[9] presents a methodology for performing such involved *ab initio* or semiempirical calculations and shows how the powerful group-theoretical methods can be used to make a complicated physical problem as transparent as possible. In this respect, the various formulas derived in this paper set a framework for the analysis of measurements and computation of angle- and spin-resolved photoelectron spectra in a T_d molecule, whereas the results given herein can be used as a reference point for comparing more accurate calculations.

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APPENDIX

Here we give the basis functions $\chi_{hl}^{(p)q\iota}(\mathbf{x})$ for the double-valued IR's of the extended T_d point group which is of particular interest in the present paper. This group has two one-dimensional ($p = A_1, A_2$; $\tau = 1$), one two-dimensional ($p = E$; $\tau = 1-2$), and two three-dimensional ($p = T_1, T_2$; $\tau = 1-3$) single-valued IR's. The GH, $X_{hl}^{p\tau}(\hat{\mathbf{r}})$, for these IR's are already given in Appendix 3 in Ref. 20. A spin-$\frac{1}{2}$ function belongs to the $E_{1/2}$ double-valued IR of the extended T_d group. On the inclusion of SOI, the double-valued representations of this group are therefore given by[11–13]

$$A_1 \otimes E_{1/2} = E_{1/2}\ ,$$

$$A_2 \otimes E_{1/2} = E_{5/2}\ ,$$

$$E \otimes E_{1/2} = G_{3/2}\ ,$$

$$T_1 \otimes E_{1/2} = E_{1/2} \oplus G_{3/2}\ ,$$

$$T_2 \otimes E_{1/2} = E_{5/2} \oplus G_{3/2}\ ,$$

where both $E_{1/2}$ and $E_{5/2}$ are two dimensional, and $G_{3/2}$ is four dimensional. The bases or symmetry-adapted functions for these IR's are as follows.[15]

(1) For $p = A_1$, $q = E_{1/2}$, $\iota = 1-2$,

$$\chi_{hl}^{(p)q\iota=1} = \alpha X_{hl}^{p\tau=1}\ ,$$

$$\chi_{hl}^{(p)q\iota=2} = \beta X_{hl}^{p\tau=1}\ .$$

(2) For $p = A_2$, $q = E_{5/2}$, $\iota = 1-2$,

$$\chi_{hl}^{(p)q\iota=1} = \alpha X_{hl}^{p\tau=1}\ ,$$

$$\chi_{hl}^{(p)q\iota=2} = \beta X_{hl}^{p\tau=2}\ .$$

(3) For $p = E$, $q = G_{3/2}$, $\iota = 1-4$,

$$\chi_{hl}^{(p)q\iota=1} = \alpha X_{hl}^{p\tau=1}\ ,$$

$$\chi_{hl}^{(p)q\iota=2} = \alpha X_{hl}^{p\tau=2}\ ,$$

$$\chi_{hl}^{(p)q\iota=3} = \beta X_{hl}^{p\tau=1}\ ,$$

$$\chi_{hl}^{(p)q\iota=4} = \beta X_{hl}^{p\tau=2}\ .$$

(4) For $p = T_1$, $q = E_{1/2}$, $\iota = 1-2$,

$$\chi_{hl}^{(p)q\iota=1} = \beta(X_{hl}^{p\tau=1} - iX_{hl}^{p\tau=2}) - \alpha X_{hl}^{p\tau=3}\ ,$$

$$\chi_{hl}^{(p)q\iota=2} = \alpha(X_{hl}^{p\tau=1} + iX_{hl}^{p\tau=2}) + \beta X_{hl}^{p\tau=3}\ .$$

(5) For $p = T_1$, $q = G_{3/2}$, $\iota = 1-4$,

$$\chi_{hl}^{(p)q\iota=1} = -\beta(X_{hl}^{p\tau=1} - iX_{hl}^{p\tau=2}) - 2\alpha X_{hl}^{p\tau=3}\ ,$$

$$\chi_{hl}^{(p)q\iota=2} = \sqrt{3}\beta(X_{hl}^{p\tau=1} + iX_{hl}^{p\tau=2})\ ,$$

$$\chi_{hl}^{(p)q\iota=3} = -\alpha(X_{hl}^{p\tau=1} + iX_{hl}^{p\tau=2}) + 2\beta X_{hl}^{p\tau=3}\ ,$$

$$\chi_{hl}^{(p)q\iota=4} = \sqrt{3}\alpha(X_{hl}^{p\tau=1} - iX_{hl}^{p\tau=2})\ .$$

(6) For $p = T_2$, $q = E_{5/2}$, $\iota = 1-2$,

$$\chi_{hl}^{(p)q\iota=1} = \beta(X_{hl}^{p\tau=1} - iX_{hl}^{p\tau=2}) - \alpha X_{hl}^{p\tau=3}\ ,$$

$$\chi_{hl}^{(p)q\iota=2} = \alpha(X_{hl}^{p\tau=1} + iX_{hl}^{p\tau=2}) + \beta X_{hl}^{p\tau=3}\ .$$

(7) For $p = T_2$, $q = G_{3/2}$, $\iota = 1-4$,

$$\chi_{hl}^{(p)q\iota=1} = \sqrt{3}\beta(X_{hl}^{p\tau=1} + iX_{hl}^{p\tau=2})\ ,$$

$$\chi_{hl}^{(p)q\iota=2} = \beta(X_{hl}^{p\tau=1} - iX_{hl}^{p\tau=2}) + 2\alpha X_{hl}^{p\tau=3}\ ,$$

$$\chi_{hl}^{(p)q\iota=3} = \sqrt{3}\alpha(X_{hl}^{p\tau=1} - iX_{hl}^{p\tau=2})\ ,$$

$$\chi_{hl}^{(p)q\iota=4} = \alpha(X_{hl}^{p\tau=1} + iX_{hl}^{p\tau=2}) - 2\beta X_{hl}^{p\tau=3}\ .$$

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