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Auger-electron spectroscopy of molecules: Circular dichroism in angular correlation with photoelectrons from rotating linear molecules

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In this paper, we report a study of circular dichroism in angular correlation between photoelectrons and Auger electrons emitted sequentially from a free, gaseous, linear molecule whose rotational motion has also been taken into account. The outgoing electrons are observed without their spins. The photon-propagation and electron-detection configurations, along with other conditions, have been specified wherein dichroic effects do not necessarily vanish in one-photon, two-step, double ionization of rotating linear molecules. The analysis is presented in terms of both the state multipoles and the photoionization matrix elements. It is completely general and is independent of any particular dynamical description of the photoabsorption as well as Auger emission processes.

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I. INTRODUCTION

Recently, we [1,2] have predicted chirality in the integrated as well as the differential Auger currents emitted following absorption of circularly polarized (CP) light in the electric-dipole ($E1$) approximation in an achiral, linear molecule. The conditions for the presence of circular dichroism in Auger electron spectroscopy (CDAES) are not only entirely different but also less stringent than those required in other scenarios where dichroic effects are hitherto found to exist and very much depend upon the symmetry of the nuclear field experienced by the escaping Auger electron. This field in linear molecules is always cylindrically symmetric. For the CDAES in such molecules not to be trivially zero, it is necessary [1,2] to observe spin-resolved Auger electrons, but without including either the spin-orbit interaction or the spin-rotation interaction. Nonlinear molecules, on the other hand, have neither spherical nor cylinderical symmetry. The CDAES in these molecules was therefore found [2] to be present even in spin-resolved Auger electrons with a simple $\cos\theta_a$ distribution. Here θ_a is the angle between the direction of incidence of the CP light and that of ejection of the Auger electron.

Chandra and Chakraborty [2] have shown the presence of circular dichroism (CD) also in the angular correlation between Auger and photoelectrons without analyzing orientation of their spins. The target may be either a linear or a nonlinear molecule that belongs to one of the 32 point groups. This circular dichroism in one-photon, two-step, double ionization [i.e., the circular dichroism in double ionization (CDDI)] is very different from that studied by Berakdar and Klar [3(a)] and Berakdar *et al.* [3(b)] for atoms and by Chandra [4] for molecules in one-photon, one-step, double ionization [i.e., circular dichroism in double photoionization (CDDPI)]. In CDDI, the emission of the first electron by light interacting with the target in the form of a vector operator in the $E1$ approximation is followed by the ejection of the Auger electron. But in CDDPI, both electrons are emitted simultaneously by the $E1$ interaction. Due to the presence of an intermediate state of the photoion AB^{+*} in the process (1) in CDDI, unlike in CDDPI, the excess photon energy is not shared continuously between the kinetic energies of two ejected electrons. The Auger electrons will have the same kinetic energies as long as the states of AB^{+*} and of AB^{2+} in (1) remain unchanged, whatever the frequency of the incident light. CDDI has already been theoretically studied by Kammerling and Schmidt [5] for Xe and by Schmidt [6] for Mg.

Chandra and Chakraborty [2], in their work on CDDI, did not take nuclear rotation into account. But recent advances [7-10] in high-resolution electron spectroscopic techniques have made it possible to obtain rotationally resolved spectra produced in photoionization of "light" molecules such as H_2, N_2, O_2, CO, and NO. These high-resolution electron spectrometers can possibly be used in future CDDI experiments on rotating linear molecules as well.

In the next section we therefore develop theoretical expressions for CDDI in rotating linear molecules using parity adapted wave functions [11] in Hund's coupling schemes [12] (a) and (b). For both of these schemes, two different but equivalent CDDI expressions are derived, one in rotational state multipoles [13] and the other in $E1$ amplitudes. The properties of CDDI are also discussed therein. In Sec. III we present explicit formulas for CDDI applicable to any linear molecule with some specific values of the total angular momentum J and J_f of AB^{+*}, and AB^{2+}, respectively, in (1). The conclusion of this CDDI work is presented in Sec. IV.

II. THEORY FOR CIRCULAR DICHROISM

Let us consider the angular distribution of photoelectrons (e_p) emitted in

$$h\nu_r + AB(J_0M_0p_0) \rightarrow AB^{+*}(JMp) + e_p(\vec{k}_p) \qquad (1a)$$

and observed along with the Auger electrons (e_A) coming out in the subsequent process

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$$AB^{+*}(JMp) \rightarrow AB^{2+}(J_fM_fp_f)+e_A(\vec{k}_A) \; . \tag{1b}$$

Here AB^{2+} is a doubly charged molecular ion left after the radiationless decay of the excited photoion AB^{+*} formed in the process (1a) in a rotating linear molecule AB belonging to either the $C_{\infty v}$ or the$D_{\infty h}$ point group. $|J_0M_0p_0\rangle$, $|JMp\rangle$, and $|J_fM_fp_f\rangle$ in (1) are the molecular states of AB, AB^{+*}, and AB^{2+}, respectively. ($\vec{J}_0\hbar$, $\vec{J}\hbar$, $\vec{J}_f\hbar$) are the total angular momenta of these states, ($M_0\hbar$, $M\hbar$, $M_f\hbar$) are the respective projections of these angular momenta on the space-fixed quantization axis, and (p_0,p,p_f) are the parities [11] of the three states respectively.

The space-fixed quantization axis is nothing but the polar axis of our space (or photon) frame of references taken to be along the direction of propagation of the unpolarized (UP) or circularly polarized (CP) ionizing light. However, if the light incident in (1a) is plane polarized (PP), the direction of its electric vector then defines the polar axis of the space frame. Further, $\vec{k}_p(k_p,\hat{\vec{k}}_p(\theta_p,\phi_p))$ and $\vec{k}_A(k_A,\hat{\vec{k}}_A(\theta_A,\phi_A))$ are propagation vectors of the photoelectron and of the Auger electron ejected with energies $\epsilon_p=\hbar^2k_p^2/2m$ from AB in (1a) and with energy $\epsilon_A=\hbar^2k_A^2/2m$ from AB^{+*} in (1b), respectively.

The cross section for the angle-resolved double-ionization process (1) is given by [14]

$$\frac{d^2\sigma_{Ap}(m_r)}{d\hat{\vec{k}}_A d\hat{\vec{k}}_p}=K_{Ap}\sum_{\substack{M,M'\\ \mu_A,M_f}}\langle J_fM_fp_f;\vec{k}_A,\hat{\vec{u}}_A\mu_A|F_A|JMp\rangle\langle J_fM_fp_f;\vec{k}_A,\hat{\vec{u}}_A\mu_A|F_A|JM'p\rangle^*\rho_p(JMM';1m_r;\vec{k}_p) \; . \tag{2}$$

Here K_{Ap} is a constant, $F_A=V_c\sqrt{m/\hbar^2}$ is the Auger transition operator with V_C the interelectronic Coulomb interaction, which is a scalar, and

$$\rho_p(JMM';1m_r;\vec{k}_p)$$
$$=\sum_{K,Q}(-1)^{J-M}\sqrt{2K+1}\begin{bmatrix} J & J & K \\ M & -M' & -Q \end{bmatrix}$$
$$\times\langle T(J;1m_r;\vec{k}_p)^{\dagger}_{KQ}\rangle \tag{3}$$

is the density matrix describing the first step corresponding to the photoionization process (1a) in the electric dipole ($E1$) approximation in terms of the state multipoles [13] $\langle T(J;1m_r;\vec{k}_p)^{\dagger}_{KQ}\rangle$. The polarization of radiation absorbed in (1a) is represented by the parameter m_r in expressions (2) and (3) and elsewhere in this article. $m_r=0$ for PP and $m_r=\pm1$ for CP light; the cross section (2) needs to be averaged over $m_r=\pm1$ for UP radiation. The distribution (2) has been summed over the projection μ_A (along $\hat{\vec{u}}_A$) of the undetected spin of the Auger electron.

If E_0, E, and E_f are the respective energies of the molecular states of AB, AB^{+*}, and AB^{2+} involved in (1), then the kinetic energy of the photoelectron is $\epsilon_p=h\nu_r-(E-E_0)$ and that of the Auger electron is $\epsilon_A=E_f-E$. The kinetic energy ϵ_p will change with the energy $h\nu_r$ of the photon absorbed in (1a) even for the same states $|J_oM_op_o\rangle$ and $|JMp\rangle$ of AB and AB^{+*}, respectively. But the Auger electron will come out with the same energy ϵ_A as long as neither E nor E_f changes. Thus the angular correlation function (2) is differential in three variables, namely, $\hat{\vec{k}}_A$, $\hat{\vec{k}}_p$, and ϵ_p.

The Auger decay matrix element $\langle J_fM_fp_f;\vec{k}_A,\hat{\vec{u}}_A\mu_A|F_A|JMp\rangle$ needed in (2) is already available to us from Eq. (I7) [15] for Hund's coupling scheme (a) and from Eq. (I16) for scheme (b). In order to obtain the angular correlation functions between the two electrons ejected in the process (1) in Hund's cases (a) and (b), we substitute the pairs of equations (3), (I7) and (3), (I16), respectively, in the expression (2). The resulting two expressions, one each in coupling schemes (a) and (b), for double-ionization cross sections can be shown [14], after some simplifications to have identical geometrical but, of course, different dynamical factors. Both of these are therefore readily represented by a single function of the form [14]

$$\frac{d^2\sigma_{Ap}(m_r)}{d\hat{\vec{k}}_A d\hat{\vec{k}}_p}=(-1)^{J+J_f-1/2}(4\pi)^{-1/2}$$
$$\times\sum_{l_A,l'_A,j_A,j'_A}\sum_{K,Q}\begin{bmatrix} l_A & l'_A & K \\ 0 & 0 & 0 \end{bmatrix}\begin{Bmatrix} l_A & l'_A & K \\ j'_A & j_A & \frac{1}{2} \end{Bmatrix}\begin{Bmatrix} J & J & K \\ j'_A & j_A & J_f \end{Bmatrix}\Theta^{(1)}_{KQ}(J;m_r;\vec{k}_p)A_{l_Aj_A}A^*_{l'_Aj'_A}Y^Q_K(\hat{\vec{k}}_A) \; . \tag{4}$$

Here

$$\Theta^{(1)}_{KQ}(J;m_r;\vec{k}_p)=(2J+1)\langle T(J;m_r;\vec{k}_p)^{\dagger}_{KQ}\rangle\sigma_A/A \; . \tag{5}$$

The "reduced" Auger amplitudes $A_{l_Aj_A}$ present in (4) and the quantities A present in (5) are obtained from Eqs. (I8) and (I8′) in Hund's case (a) and from Eqs. (I17) and (I17′) in Hund's case (b). The integrated Auger intensity σ_A, needed in (5), has also been defined in paper I for both the schemes. The state multipoles $\langle T(J;m_r;\vec{k}_p)^{\dagger}_{KQ}\rangle$ occurring in (5) are taken from Appendixes A and B for coupling schemes (a) and (b), respectively.

The circular dichroism in one-photon, two-step, double-ionization process (1) in a rotating linear molecule is readily obtained by substituting (4) in

$$\frac{d^2\sigma_{\mathrm{CD}}}{d\hat{\vec{k}}_A d\hat{\vec{k}}_p}=\frac{d^2\sigma_{Ap}(m_r=+1)}{d\hat{\vec{k}}_A d\hat{\vec{k}}_p}-\frac{d^2\sigma_{Ap}(m_r=-1)}{d\hat{\vec{k}}_A d\hat{\vec{k}}_p} ,$$

yielding

$$\frac{d^2\sigma_{\mathrm{CD}}}{d\hat{\vec{k}}_A d\hat{\vec{k}}_p}=(-1)^{J+J_f-1/2}\sum_{\substack{l_A,j_A\\ l'_A,j'_A}}\sum_{KQ}\begin{bmatrix} l_A & l'_A & K\\ 0 & 0 & 0\end{bmatrix}\begin{Bmatrix} l_A & l'_A & K\\ j'_A & j_A & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix} J & J & K\\ j'_A & j_A & J_f\end{Bmatrix}A_{l_Aj_A}$$
$$\times A^{*}_{l'_Aj'_A}\,\Theta^{(1)}_{KQ}(J;\vec{k}_p)_{\mathrm{CD}}Y^{Q}_{K}(\hat{\vec{k}}_A) , \tag{6a}$$

where

$$\Theta^{(1)}_{KQ}(J;\vec{k}_p)_{\mathrm{CD}}=\Theta^{(1)}_{KQ}(J;m_r=+1;\vec{k}_p)-\Theta^{(1)}_{KQ}(J;m_r=-1;\vec{k}_p) . \tag{6b}$$

Equations (6) give us CDDI in terms of the state multipoles of the photoion AB^{+*} before its Auger decay. In order to obtain an expression for CDDI that contains $E1$ photoionization amplitudes, we substitute in (6b) the definition (5), along with appropriate expressions, for $\langle T(J;m_r;\vec{k}_p)^{\dagger}_{KQ}\rangle$ taken from Eq. (A7). After simplifications we get

$$\frac{d^2\sigma_{\mathrm{CD}}}{d\hat{\vec{k}}_A d\hat{\vec{k}}_p}=(-1)^{-J_0-J_f}(2J+1)\frac{\sigma_A}{2\pi A}\left[\tfrac{3}{2}\right]^{1/2}K_p$$
$$\times\sum_{\substack{l_A,l'_A\\ j_A,j'_A}}\sum_{\substack{l_p,l_t,J_s\\ l'_p,l'_t,J'_s}}\sum_{L_p,K,Q}(-1)^{l_p+l'_t}\sqrt{(2L_p+1)(2K+1)}\begin{bmatrix} l_A & l'_A & K\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix} l_p & l'_p & L_p\\ 0 & 0 & 0\end{bmatrix}$$
$$\times\begin{bmatrix} K & L_p & 1\\ Q & -Q & 0\end{bmatrix}\begin{Bmatrix} J & J & K\\ j'_A & j_A & J_f\end{Bmatrix}\begin{Bmatrix} l_A & l'_A & K\\ j'_A & j_A & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix} J & J & K\\ J'_s & J_s & \frac{1}{2}\end{Bmatrix}$$
$$\times\begin{Bmatrix} l_t & l'_t & K\\ J'_s & J_s & J_0\end{Bmatrix}\begin{Bmatrix} l_p & l'_p & L_p\\ l_t & l'_t & K\\ 1 & 1 & 1\end{Bmatrix}Y^{Q}_{K}(\hat{\vec{k}}_A)Y^{-Q}_{L_p}(\hat{\vec{k}}_p)A_{l_Aj_A}A^{*}_{l'_Aj'_A}$$
$$\times\langle (Js_p)J_s;l_p|F(l_t)|J_0;1\rangle\langle (Js_p)J'_s;l'_p|F(l'_t)|J_0;1\rangle^{*} \tag{7}$$

for both Hund's coupling scheme (a) as well as (b), with the corresponding Auger decay matrix element $A_{l_Aj_A}$ taken from paper I. The reduced amplitude $\langle (Js_p)J_s;l_p|F(l_t)|J_0;1\rangle$ is supplied by Eq. (A4) for Hund's case (a) and by Eq. (B3) for case (b).

Introducing the bipolar harmonics [16]

$$\mathcal{Y}^{KL_p}_{10}(\hat{\vec{k}}_A,\hat{\vec{k}}_p)=(-1)^{L_p-K}\sqrt{3}\sum_{Q}\begin{bmatrix} K & L_p & 1\\ Q & -Q & 0\end{bmatrix}Y^{Q}_{K}(\hat{\vec{k}}_A)Y^{-Q}_{L_p}(\hat{\vec{k}}_p) , \tag{8}$$

the CDDI (7) can be written as

$$\frac{d^2\sigma_{\mathrm{CD}}}{d\hat{\vec{k}}_A d\hat{\vec{k}}_p}=\sum_{K,L_p}C_{KL_p}(J_0JJ_f;k_Ak_p)\mathcal{Y}^{KL_p}_{10}(\hat{\vec{k}}_A,\hat{\vec{k}}_p) , \tag{9a}$$

with

$$C_{KL_p}(J_0JJ_f;k_Ak_p)=(-1)^{-J_0-J_f}(2J+1)\frac{\sigma_a}{2\pi A\sqrt{2}}K_p$$

$$\times\sum_{\substack{l_A,l'_A\\ j_A,j'_A}}\sum_{\substack{l_p,l_t,J_s\\ l'_p,l'_t,J'_s}}(-1)^{l_t+l'_p}\sqrt{(2K+1)(2L_p+1)}\begin{pmatrix} l_A & l'_A & K\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_p & l'_p & L_p\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} J & J & K\\ j'_A & j_A & J_f\end{Bmatrix}$$

$$\times\begin{Bmatrix} l_p & l'_A & K\\ j'_A & j_A & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix} J & J & K\\ J'_s & J_s & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix} l_t & l'_t & K\\ J'_s & J_s & J_0\end{Bmatrix}\begin{Bmatrix} l_p & l'_p & L_p\\ l_t & l'_t & K\\ 1 & 1 & 1\end{Bmatrix}A_{l_Aj_A}A^*_{l'_Aj'_A}$$

$$\times\langle (Js_p)J_s;l_p|F(l_t)|J_0;1\rangle\langle (Js_p)J'_s;l'_p|F(l'_t)|J_0;1\rangle^* . \tag{9b}$$

Since we are using parity adapted wave functions [11] for all of the molecular states involved in the process (1) and the quantum numbers (J_o,J,J_f) have definite values, both K and L_p are even, as well as finite, positive integers in Eqs. (4)–(7) and (9). Hence the CDDI expressions obtained in this paper contain a limited number of harmonics [17] only of even order in the directions of propagation $\hat{k}_p$ and $\hat{k}_A$ of the photoelectrons and the Auger electrons, respectively. One can readily show that Eqs. (7) and (9) have the following properties.

(i) Let us specialize (8) to a coplanar experimental configuration wherein detectors for Auger electrons and photoelectrons and the polar axis of the laboratory frame (which is along the direction of incidence of the CP radiation) are in a single plane, i.e., $|\phi_A-\phi_p|=n\pi$ with $n=0-2$. We find that the CDDI (9) becomes zero. The CD is absent in a coplanar experimental geometry in double ionization also of atoms as the atomic states also are, in general, parity eigenstates. In both of these cases one has only the directions of two outgoing electrons plus the axial vector of circular polarization. Therefore, no handedness exists if all three vectors are in a single plane, hence the absence of CDDI in the coplanar configuration. Although CDDI does not exist in coplanar arrangements for atoms and linear molecules, the angular correlation between the photoelectrons and the Auger electrons is, nevertheless, not necessarily zero even in this case [14,18,19].

(ii) $d^2\sigma_{\rm CD}/d\hat{k}_A d\hat{k}_p$ will vanish identically where the angular momentum J of the excited photoion AB^{+*} in (1) is less than one. In that case, the allowed even value of K will only be zero from the triangular condition $\Delta(J,J,K)$, which needs to be satisfied in order for the first and third 6-j symbols in (7) to exist. But L_p also should be even. The third 3-j symbol present in (7) will then identically vanish. This result will hold for all directions of $\hat{k}_p$ and $\hat{k}_A$. However, this property of CDDI in rotating linear molecules is not surprising for the simple reason [14] that when $J<1$, the angular correlation between Auger electrons and photoelectrons from a rotating linear molecule is completely isotropic. An isotropic distribution will not naturally exhibit any dichroic effect.

Both results (i) and (ii) are applicable in either of the coupling schemes being considered by us.

III. APPLICATION

Let us derive explicit expressions for CDDI in a rotating linear molecule when the total angular momentum J_f of the doubly ionized residue AB^{2+} after Auger decay is 0. For the first 6-j symbol in (7) not to be zero, the triangular relations $\Delta(J,j_A,J_f)$ and $\Delta(J,j'_A,J_f)$ must be satisfied. As both j_A $(=l_A\pm\frac{1}{2})$ and j'_A $(=l'_A\pm\frac{1}{2})$ are half integers, the angular momentum J of the photoion AB^{+*} must also be half integers. Then, according to the discussion presented in Sec. II, the minimum allowed value of J for CDDI not to vanish identically is $\frac{3}{2}$. The third 6-j symbol in (7) consequently gives $J_s=1$ and 2. This, in other words, means that the total angular-momentum quantum number J_o of AB in (1) has to be an integer, for l_t defined in (A1) cannot be a half integer. We take in this application, for simplicity, the minimum allowed value $J_o=0$.

It is obvious that $J=\frac{3}{2}$ in Hund's coupling scheme (a) means [20] that the spin of AB^{+*} is given by $S\geq|-\Lambda+\frac{3}{2}|$. Hence some of the possible electronic states of AB^{+*} are ${}^{4,6,8,\ldots}\Sigma$ (i.e., ${}^4\Sigma$, ${}^6\Sigma,\ldots$), ${}^{(2,4,6,\ldots)}\Pi$, ${}^{(2,4,6,\ldots)}\Delta$, etc. In Hund's coupling scheme (b), on the other hand, the states [20] ${}^4\Sigma$ for $N=0$; ${}^{(2,4,6)}\Sigma$ and ${}^{(2,4,6)}\Pi$ for $N=1$; ${}^{(2,4,6,8)}\Sigma$, ${}^{(2,4,6,8)}\Pi$, and ${}^{(2,4,6,8)}\Delta$ for $N=2$; etc. of AB^{+*} will have $J=\frac{3}{2}$. Similarly, the coupling (a) electronic states of AB that will have $J=0$ and of AB^{2+} with $J_f=0$ are ${}^{(1,3,5,7,\ldots)}\Sigma$, ${}^{(3,5,7,\ldots)}\Pi$, ${}^{(5,7,9,\ldots)}\Delta$, etc., whereas, the coupling (b) states of both AB and AB^{2+} are ${}^1\Sigma$, ${}^3(\Sigma,\Pi)$, ${}^5(\Sigma,\Pi,\Delta)$, etc., for N_o and $N_f=0,1,2,\ldots$, etc., respectively.

From the first 6-j symbol in (7), we find j_A and $j'_A=\frac{3}{2}$, giving, in view of the second 6-j symbol, l_A and $l'_A=1$ or 2. That is, only a single (p or d) partial wave of the Auger electron contributes in the present example of double ionization (DI). The first 6-j symbol also gives $K=0-3$. However, because of the first and third 3-j symbols, K can be neither zero or odd. Therefore, the only permissible value of K in the present case is $K=2$. In addition to this, the third and fourth 6-j symbols present in (7), on the other hand, yield $l_t,l'_t=1$ and 2. An application of the trangular condition implied in the definition (A1) gives $l_p,l'_p=0-3$. However, it is obvious from the second and third 3-j symbols occurring in (7) that L_p, and hence l_p and l'_p, cannot be zero. Then we obviously have $l_p,l'_p=2$ or 1,3 with $L_p=2$ only. Therefore, in the application being considered (with $J_o,J_f=0$ and $J=\frac{1}{2}$), the CD (7) will have spherical harmonics $Y_2^Q(\hat{\vec{k}}_A)$ and $Y_2^{-Q}(\hat{\vec{k}}_p)$ only. The CDDI is finally given by, for l_p, $l'_p=2$; $l_A,l'_A=1$ or 2,

$$\frac{d^2\sigma_{\rm CD}}{d\hat{\vec{k}}_A\,d\hat{\vec{k}}_p}=i\frac{\sigma_A K_p}{9600\pi^2}[\langle(\tfrac{3}{2}s_p)1;2|F(1)|0;1\rangle \times\langle(\tfrac{3}{2}s_p)2;2|F(2)|0;1\rangle^*-{\rm c.c.}] \times f(\hat{\vec{k}}_A,\hat{\vec{k}}_p) \qquad (10a)$$

and, for $l_p,l'_p=1$ and 3; l_A, $l'_A=1$ or 2,

$$\frac{d^2\sigma_{\rm CD}}{d\hat{\vec{k}}_A\,d\hat{\vec{k}}_p}=i\frac{\sigma_A K_p}{320\pi^2}\left\{\frac{1}{2\sqrt{70}}[\langle(\tfrac{3}{2}s_p)1;1|F(1)|0;1\rangle\langle(\tfrac{3}{2}s_p)2;3|F(2)|0;1\rangle^*-{\rm c.c.}] +\frac{1}{10\sqrt{14}}[\langle(\tfrac{3}{2}s_p)2;1|F(2)|0;1\rangle\langle(\tfrac{3}{2}s_p)2;3|F(2)|0;1\rangle^*-{\rm c.c.}] -\frac{1}{3\sqrt{20}}[\langle(\tfrac{3}{2}s_p)1;1|F(1)|0;1\rangle\langle(\tfrac{3}{2}s_p)2;1|F(2)|0;1\rangle^*-{\rm c.c.}]\right\} f(\hat{\vec{k}}_A,\hat{\vec{k}}_p)\ , \qquad (10b)$$

with

$$f(\hat{\vec{k}}_A,\hat{\vec{k}}_p)=2\sin^2\theta_A\sin^2\theta_p\sin2(\phi_A-\phi_p) +\sin2\theta_A\sin2\theta_p\sin(\phi_A-\phi_p)\ . \qquad (11)$$

Thus both (10a) and (10b) depend on the Auger decay dynamics only to the extent of the integrated Auger intensity σ_A. This is a consequence of the fact, as shown in the preceding paragraph, that only a single partial wave is required to represent the Auger electron in the present example. Another consequence of this is that CDDI is split in two, rather than in four, continua corresponding to l_p,l'_p even and odd. The angular part (11) of CDDI (10a) and (10b) is identical for the reasons explained in the preceding paragraph. Also $f(\hat{\vec{k}}_A,\hat{\vec{k}}_p)=0$ for $\phi_A-\phi_p=0$, π, and 2π, that is, CDDI (10) vanishes identically for coplanar incident ionizing radiation, Auger electrons, and photoelectrons. This result is in accordance with property (ii) of CDDI in rotating linear molecules discussed previously in this paper.

The reduced amplitudes $\langle(Js_p)J_s;\ l_p|F(l_t)|J_0;1\rangle$ used in (10) are given by Eq. (A4) in Hund's coupling scheme (a) and by Eq. (B3) in scheme (b). These amplitudes are completely determined by the allowed transitions only, that is, it is the electric dipole $E1$ operator that makes transitions involved in (A4) and (B3) take place. Thus the CD effect in the present example of DI is completely determined, apart from the total Auger intensity σ_A, by the photoionization dynamics in the $E1$ approximation.

Unlike the forbidden transitions [caused by the magnetic dipole ($M1$), the electric quadrupole ($E2$), the magnetic quadrupole ($M2$), etc., operators], the allowed $E1$ transitions are usually readily observable with modern experimental facilities. In fact, Kammerling and Schmidt [5] and Schmidt [6] have already calculated CDDI in atoms and found it to be measurable by the existing experimental apparatus. The structure of the theoretical expressions describing CDDI in atoms and in rotating linear molecules is identical [18]. For these reasons, it is natural to conclude that the CDDI effect even in rotating linear molecules should be sufficiently large so that, similar to the atomic case [5,6], one is able to observe it with modern experimental facilities.

IV. CONCLUSION

In this paper we have set up a methodology and developed a framework for studying dichroic effects in one-photon, two-step, double ionization of a rotating linear molecule. Expressions for CDDI in terms of both state multipoles as well as in terms of $E1$ ionization amplitudes have been derived. Using the parity adapted molecular states, both of Hund's coupling schemes (a) and (b) are considered. An analysis of these expressions shows that the CDDI will necessarily be zero if the total angular momentum of the intermediate state of the excited photoion before Auger decay is less than one. The other result is that the CDDI vanishes where the detected Auger electrons and the photoelectrons and the CP ionizing radiation are in a single plane. This result is applicable whether or not rotation of the nuclei in a linear molecule has been taken into account.

Because CDDI expressions usually contain fewer terms than otherwise, it is therefore at least theoretically easier to study electron correlation by investigating dichroic effects. These can be used to extract information on state multipoles as well as to calibrate the degree of circular polarization of x rays.

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APPENDIX A: ROTATIONAL STATE MULTIPOLES FOR THE PROCESS (1a) IN A ROTATING LINEAR MOLECULE IN HUND'S COUPLING SCHEME (a)

In this appendix we obtain density matrix and state multipoles used in the various expressions in Sec. II of the present paper in Hund's coupling scheme (a); Appendix B contains the same quantities in the scheme (b). The desired expressions are derived in terms of the angular-momentum transfer

$$\vec{l}_t \equiv \vec{l}_r - \vec{l}_p = \vec{J}_s \;(\equiv \vec{J} + \vec{s}_p) - \vec{J}_0 \; . \tag{A1}$$

Here $\vec{l}_r$ ($|\vec{l}_r|=1$ in the $E1$ approximation) is the photon angular momentum, $\vec{l}_p$ and $\vec{s}_p$ ($|\vec{s}_p|=\frac{1}{2}$) are, respectively, the orbital and the spin angular-momentum vectors of the photoelectron in the process (1a). The vector $\vec{l}_t$ was originally introduced by Fano and Dill [21–23] to simplify the mathematical structure and hence provide better physical insight into the angle-resolved photoelectron spectroscopy of atoms and molecules. The definition (A1) is appropriate for those experiments on photoelectron spectroscopy that do not analyze the spin of the observed photoelectron ejected in the $E1$ approximation.

The density matrix and state multipoles obtained in Ref. [14] for studying angle and spin correlation between the photoelectron and the Auger electron are based, on the other hand, on the angular-momentum transfer

$$\vec{j}_t = \vec{l}_r - \vec{j}_p \;(\equiv \vec{l}_p + \vec{s}_p) = \vec{J} - \vec{J}_0 \; ,$$

which is different from that defined in (A1). This $\vec{j}_t$ was introduced by one of us [24] to study angle- and spin-resolved photoelectron spectroscopy of atoms and molecules.

The density matrix we need is given by

$$\rho_p(JMM';1m_r;\vec{k}_p) = (2J_0+1)^{-1} K_p \sum_{\mu_p, M_0} \langle JMp;\vec{k}_p;\hat{\vec{u}}_p\mu_p|F_p|J_0M_0p_0;1m_r\rangle \langle JM'p;\vec{k}_p;\hat{\vec{u}}_p\mu_p|F_p|J_0M_0p_0;1m_r\rangle^* \; . \tag{A2}$$

Here angular brackets are the $E1$ amplitudes for the process (1a), the constant K_p and the dipole operator F_p are defined in Ref. [25]. Equation (A2) has been summed over μ_p, which is the projection of $\vec{s}_p$ in direction $\hat{\vec{u}}_p$, to account for the fact that the photoelectron's spin remains undetected.

On substituting (IA2) and (IA4), alongwith (IA3), we find that each of the two photoionization matrix elements in (A2) will contain, in addition to other things, an integral over the product of $\mathcal{D}^J \mathcal{D}^{l_p} \mathcal{D}^{1/2} \mathcal{D}^{J_0} \mathcal{D}^1$ in Hund's case (a). Each of the $\mathcal{D}$'s in this product is a rotational harmonics [17]. In order to introduce l_t according to the definition (A1), we couple $\mathcal{D}^{J_0}$ with the combination of $\mathcal{D}^J \mathcal{D}^{1/2}$ using the Clebsch-Gordan series [17] in 3-j symbols. The two remaining harmonics $\mathcal{D}^{l_p}$, $\mathcal{D}^1$ are combined separately. This procedure reduces the above-mentioned integrand into a sum of the product of six 3-j symbols and two rotational harmonics, in addition to various other quantities. The resulting integral is then readily performed using the orthogonality [17] of rotational harmonics. This same procedure is applied also to the evaluation of the integral of the product of five rotational harmonics present in each of the three remaining terms in the $E1$ amplitude in (A2).

Use of the identity (4.16) from Ref. [20] and some other simplifications finally leads to

$$\begin{aligned}\langle JMp;\vec{k}_p;\hat{\vec{u}}_p\mu_p|F_p|J_0M_0p_0;1m_r\rangle &= (-1)^{1+m_r}\sqrt{(2J_0+1)/(2l_p+1)} \\ &\quad\times \sum_{\substack{l_p,n,\mu \\ l_t,n_t}} \sum_{J_s,N_s} (-1)^{J_s} \begin{pmatrix} J & \frac{1}{2} & J_s \\ -M & -\mu & N_s \end{pmatrix} \begin{pmatrix} J_s & J_0 & l_t \\ N_s & -M_0 & n_t \end{pmatrix} \begin{pmatrix} 1 & l_p & l_t \\ m_r & -n & n_t \end{pmatrix} \\ &\quad\times Y_{l_p}^{n}(\hat{\vec{k}}_p)\mathcal{D}^{1/2}_{\mu_p\mu}(\omega_{u_p})\langle (Js_p)J_s;l_p|F(l_t)|J_0;1\rangle \; . \end{aligned} \tag{A3}$$

The reduced amplitude in the present case is defined by

$$\begin{aligned}\langle (Js_p)J_s;l_p|F(l_t)|J_0;1\rangle &= \tfrac{1}{2}e^{i\sigma_{l_p}}(-i)^{l_p}(2J_s+1)(2l_t+1)\sqrt{(2J+1)(2l_p+1)} \\ &\quad\times \sum_{J_T}(2J_T+1)\begin{Bmatrix} J_s & J_0 & l_t \\ 1 & l_p & J_T \end{Bmatrix} \langle n\,(Js_p)J_s\Lambda\Omega p;l_p|F(J_T)|n_0J_0\Lambda_0\Omega_0p_0;1\rangle \end{aligned} \tag{A4}$$

with

$$\begin{aligned}
&\langle n(Js_p)J_s\Lambda\Omega p;l_p|F(J_T)|n_0J_0\Lambda_0\Omega_0p_0;1\rangle \\
&\quad=[1+(-1)^{1/2+l_p+J_0-J+p+p_0}] \\
&\qquad\times\sum_{m,\nu}\sum_{\lambda_r,M_s}(-1)^{-M_s}\begin{pmatrix} J & \frac{1}{2} & J_s \\ -\Omega & -\nu & M_s\end{pmatrix}\begin{pmatrix} l_p & J_s & J_T \\ m & M_s & M_T\end{pmatrix} \\
&\qquad\qquad\times\left[\begin{pmatrix} J_0 & 1 & J_T \\ \Omega_0 & \lambda_r & M_T\end{pmatrix}\langle n\Lambda S\Sigma\Omega;l_pm\nu|F|n_0\Lambda_0S_0\Sigma_0\Omega_0;1\lambda_r\rangle+(-1)^{p_0+2\Omega_0+M_s}\right. \\
&\qquad\qquad\left.\times\begin{pmatrix} J_0 & 1 & J_T \\ -\Omega_0 & \lambda_r & M_T\end{pmatrix}\langle n\Lambda S\Sigma\Omega;l_pm\nu|F|n_0-\Lambda_0S_0-\Sigma_0-\Omega_0;1\lambda_r\rangle\right] .
\end{aligned}\tag{A5}$$

The selection rule $\frac{1}{2}+l_p+J_0-J+p+p_0$ even is identical to that found earlier [14,15] in simplifying the photoionization matrix element present in (A2) using two different definitions, other than (A1), of the angular-momentum transfer.

In order to obtain the desired density matrix for the process (1a), we first substitute the amplitude (A3) in (A2) and carry out the sum over μ_p using the unitary property [17] of the $\mathscr{D}$'s . The resulting expression is then simplified and brought to the desired form by applying, in succession, the identities (14.42) from [26], (4.16) from [20], (4.6.5) from [17], (14.42) from [26], and (10) from [16], p. 464. We finally get

$$\begin{aligned}
&\rho_p(JMM';1m_r;\vec{k}_p) \\
&\quad=(-1)^{m_r-1/2}\frac{K_p}{\sqrt{4\pi}} \\
&\qquad\times\sum_{\substack{l_p,l_t,J_s,\\ l'_p,l'_t,J'_s}}\sum_{\substack{L_p,L_r\\ A,M_L}}(-1)^{l_p+l'_t-J_0+M}(2L_r+1)(2A+1)\sqrt{2L_p+1}\begin{pmatrix} l_p & l'_p & L_p \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} 1 & 1 & L_r \\ -m_r & m_r & 0\end{pmatrix} \\
&\qquad\qquad\times\begin{pmatrix} J & J & A \\ M & -M' & M_L\end{pmatrix}\begin{pmatrix} L_p & A & L_r \\ -M_L & M_L & 0\end{pmatrix}\begin{Bmatrix} J & J & A \\ J'_s & J_s & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix} l_t & l'_t & A \\ J'_s & J_s & J_0\end{Bmatrix}\begin{Bmatrix} l_p & l'_p & L_p \\ l_t & l'_t & A \\ 1 & 1 & L_r\end{Bmatrix} \\
&\qquad\qquad\times Y_{L_p}^{M_L}(\hat{\vec{k}}_p)\langle(Js_p)J_s;l_p|F(l_t)|J_0;1\rangle\langle(Js_p)J'_s;l'_p|F(l'_t)|J_0;1\rangle^* .
\end{aligned}\tag{A6}$$

In order to obtain state multipoles, we first substitute (A6) in the inverse of (3) and then simplify the resulting expression using the orthogonality [17] of 3-j symbols. This procedure yields

$$\begin{aligned}
&\langle T(J;1m_r;\vec{k}_p)^\dagger_{KQ}\rangle=(-1)^{J-J_0+m_r-1/2}\frac{K_p}{\sqrt{4\pi}} \\
&\qquad\times\sum_{\substack{l_p,l_t,J_s\\ l'_p,l'_t,J'_s}}\sum_{L_p,L_r}(-1)^{l_p+l'_t}(2L_r+1)\sqrt{(2L_p+1)(2K+1)}\begin{pmatrix} l_p & l'_p & L_p \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} 1 & 1 & L_r \\ -m_r & m_r & 0\end{pmatrix} \\
&\qquad\qquad\times\begin{pmatrix} L_p & K & L_r \\ Q & -Q & 0\end{pmatrix}\begin{Bmatrix} J & J & K \\ J'_s & J_s & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix} l_t & l'_t & K \\ J'_s & J_s & J_0\end{Bmatrix}\begin{Bmatrix} l_p & l'_p & L_p \\ l_t & l'_t & K \\ 1 & 1 & L_r\end{Bmatrix} \\
&\qquad\qquad\times Y_{L_p}^{-Q}(\hat{\vec{k}}_p)\langle(Js_p)J_s;l_p|F(l_t)|J_0;1\rangle\langle(Js_p)J'_s;l'_p|F(l'_t)|J_0;1\rangle^* .
\end{aligned}\tag{A7}$$

The highest-order multipole moment that can be determined in the present case is obviously $0\le K\le\min[2(l_p)_{\max}+2,\ 2J+1]$. The normalized statistical tensors are defined by

$$\rho_{KQ}(J;m_r;\vec{k}_p)=\sqrt{2J+1}\frac{\langle T(J;1m_r;\vec{k}_p)^\dagger_{KQ}\rangle}{\langle T(J;1m_r;\vec{k}_p)^\dagger_{00}\rangle} . \tag{A8}$$

It is obvious from Eqs. (A6) and (A7) that

$$\begin{aligned}
&\langle T(J;1m_r,\vec{k}_p)^\dagger_{00}\rangle \\
&\quad=(2J+1)^{-1/2}\sum_M\rho_p(JMM;1m_r;\vec{k}_p) \\
&\quad=(2J+1)^{-1/2}\frac{d\sigma_p(J;m_r)}{d\hat{\vec{k}}_p} .
\end{aligned}\tag{A9}$$

Here $d\sigma_p(J;m_r)/d\hat{k}_p$ is the differential photocurrent of spin-unresolved photoelectrons ejected in the process (1a). This expression can be shown to have a form identical to that given in Refs. [21–23] and in Ref. [27] in terms of an incoherent sum over the angular momentum transfer l_t.

APPENDIX B: ROTATIONAL STATE MULTIPOLES FOR THE PROCESS (1a) IN A ROTATING LINEAR MOLECULE IN HUND'S COUPLING SCHEME (b)

An expression for the $E1$ amplitude $\langle JMp;\vec{k}_p;\hat{\vec{u}}_p\mu_p|F_p|J_0M_0p_0;1m_r\rangle$ in Hund's coupling scheme (b) is readily obtained by first following the procedure described at the beginning of Appendix B in paper I. This amplitude contains, in addition to several other terms, an integral over the product of $\mathcal{D}^{l_p}\mathcal{D}^{N}\mathcal{D}^{1}\mathcal{D}^{N_0}$. On combining $\mathcal{D}^{l_p}$ with $\mathcal{D}^{1}$ and $\mathcal{D}^{N}$ with $\mathcal{D}^{N_0}$, this product reduces to a sum of the product of four 3-j symbols and two rotational harmonics. The resulting integral is readily performed using orthogonality [17] of $\mathcal{D}$ functions. After that, we apply identities (4.16) from [20] and (7) from p. 454 in Ref. [16], respectively. The next step is to perform, with the help of Eq. (3.7.9) from [17], a single sum over the magnetic quantum number M_{S_0} associated with the spin of AB in the state $|J_0M_0p_0\rangle$ in (1a). This procedure is readily repeated for the three other similar terms present in $\langle JMp;\vec{k}_p;\hat{\vec{u}}_p\mu_p|F_p|J_0M_0p_0;1m_r\rangle$. A few additional simplifications finally lead us to

$$\begin{aligned}\langle JMp;\vec{k}_p,\hat{\vec{u}}_p\mu_p|F_p|J_0M_0p_0;1m_r\rangle=&(-1)^{M-M_0+J-S+\Lambda_0+S_0+N}\\&\times\sum_{\substack{l_p,n,\mu\\l_t,n_t}}\sum_{J_s,M_s}(-i)^{l_p}e^{i\sigma_{l_p}}(-1)^{n-J_s-\mu}(2J_s+1)(2l_t+1)\sqrt{(2N_0+1)(2S_0+1)}\\&\times\sqrt{(2J_0+1)(2N+1)(2J+1)}\begin{pmatrix}1&l_p&l_t\\m_r&-n&n_t\end{pmatrix}\begin{pmatrix}J&\frac{1}{2}&J_s\\M&\mu&M_s\end{pmatrix}\\&\times\begin{pmatrix}l_t&J_0&J_s\\n_t&-M_0&M_s\end{pmatrix}\begin{Bmatrix}N&J&S\\\frac{1}{2}&S_0&J_s\end{Bmatrix}\begin{Bmatrix}J_s&J_0&l_t\\N_0&N&S_0\end{Bmatrix}Y_{l_p}^{n}(\hat{\vec{k}}_p)\mathcal{D}^{1/2}_{\mu_p\mu}(\omega_u)\\&\times\langle nN\Lambda_Np;l_p|F(l_t)|n_0N_0\Lambda_{N_0}p_0;1\rangle\end{aligned}\tag{B1}$$

with

$$\begin{aligned}&\langle nN\Lambda_Np;l_p|F(l_t)|n_0N_0\Lambda_{N_0}p_0;1\rangle\\&\quad=\tfrac{1}{2}[1+(-1)^{1+l_p+N+N_0+p+p_0}]\\&\quad\times\sum_{m,m_t\lambda_r}(-1)^m\begin{pmatrix}1&l_p&l_t\\\lambda_r&-m&m_t\end{pmatrix}\left[\begin{pmatrix}N&N_0&l_t\\\Lambda_N&-\Lambda_{N_0}&m_t\end{pmatrix}\langle n\Lambda_N;l_pm|F|n_0\Lambda_{N_0};1\lambda_r\rangle\right.\\&\qquad\qquad\left.+(-1)^{p_0}\begin{pmatrix}N&N_0&l_t\\\Lambda_N&\Lambda_{N_0}&m_t\end{pmatrix}\langle n\Lambda_N;l_pm|F|n_0-\Lambda_{N_0};1\lambda_r\rangle\right].\end{aligned}\tag{B2}$$

We now substitute (B1) and its complex conjugate in (A2), use the unitary property of the $\mathcal{D}$ functions, and apply identities (14.42) from [26], (4.16) from [20], (4.6.5) from [17], (14.42) from [26], and finally (10) from page 464 in Ref. [16], respectively. All these operations and some additional simplifications can be shown to yield Hund's coupling scheme (b) density matrix identical to that derived in the Eq. (A6) for scheme (a). But one now needs to use in Eq. (A6) the case (b) reduced amplitude

$$\begin{aligned}\langle(Js_p)J_s;l_p|F(l_t)|J_0;1\rangle=&(-i)^{l_p}e^{i\sigma_{l_p}}(-1)^{l_t-M}(2J_s+1)(2l_t+1)\\&\times\sqrt{(2N_0+1)(2S_0+1)(2N+1)(2J+1)(2l_p+1)}\begin{Bmatrix}N_0&S_0&J_0\\J_s&l_t&N\end{Bmatrix}\begin{Bmatrix}N&S&J\\\frac{1}{2}&J_s&S_0\end{Bmatrix}\\&\times\langle nN\Lambda_Np;l_p|F(l_t)|n_0N_0\Lambda_{N_0}p_0;1\rangle\,.\end{aligned}\tag{B3}$$

The expressions for state multipoles and for normalized statistical tensors in case (b) are readily obtained by merely substituting in the respective relations (A7) and (A8) the reduced amplitude (B3) in place of (A4).

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