PHYSICAL REVIEW A VOLUME 48, NUMBER 3 SEPTEMBER 1993

Auger-electron spectroscopy of molecules: Circular dichroism following photoabsorption in rotating linear molecules

N. Chandra and S. Sen
Department of Physics and Meteorology, Indian Institute of Technology, Kharagpur 721302, India

(Received 1 February 1993)

In this paper we show the existence of circular dichroism in both integrated as well as differential Auger currents produced in the decay of a vacancy created by the absorption of a circularly polarized photon in a gaseous linear molecule. It arises due to a rotational orientation of the photoexcited molecule or excited photoion. Although Auger electrons in such experiments should necessarily be observed along with their spins, neither the spin-orbit nor spin-rotation interactions, however, need to be taken into account. Circumstances when dichroic effects in such experiments are independent of photoabsorption and/or Auger-emission dynamics have also been clearly brought out by us. We have calculated the magnitude of the circular dichroism for certain realistic cases and have shown it to be of the order of magnitude of the total Auger intensity. It is proposed that circular dichroism in Auger spectroscopy provides a direct and simple method to probe rotational orientation produced by the absorption of circularly polarized light in gaseous linear molecules and to calibrate the degree of circular polarization of electromagnetic radiations over a wide range of photon energy.

PACS number(s): 33.55.−b

I. INTRODUCTION

Circular dichroism (CD) is known to imply the difference between the effects produced by the absorption of right circularly polarized (RCP) and left circularly polarized (LCP) light. It was associated for a long time only with chiral molecules. These are the objects which do not have reflection and inversion symmetries and cannot be brought into coincidence with their mirror images by rotation or translation [1]. Because this "classical" CD effect arises due to interference between the electric dipole ($E1$) and magnetic dipole ($M1$) transitions, its magnitude is therefore so small that it could not be put to use.

During the last ten years a new phenomenon involving circular dichroic effects has been theoretically [2–5] predicted and experimentally [6,7] observed. It is CD in the angular distribution (CDAD) of photoelectrons [2–7]. Here, photocurrent in a direction (i.e., the directional photocurrent) is different for RCP and LCP light. CDAD has been found for photoelectrons from nonchiral objects without the inclusion of the spin-orbit interaction (SOI). But the atomic or molecular target should now be either fixed in space (i.e., spatially fixed) [2,3(a),4(a),5,7] or polarized [3(b),4(b),5(b),6]. Because CDAD exists even in the $E1$ approximation, it is therefore orders of magnitude larger than the classical CD, and hence readily observable [3–7].

In the present article we investigate, on the other hand, the existence of dichroic effects in conditions which are not only different but also less stringent than those present in the two above-mentioned scenarios. Let us consider Auger-electron spectroscopy (AES), following photoabsorption, in its well-known two-step model. In the first step, a vacancy is created by the absorption of a photon in the $E1$ approximation in an atomic or molecular target which needs neither be polarized nor spatially fixed. This vacancy subsequently decays by ejecting an electron (called Auger electron) via the scalar, interelectronic Coulomb interaction in the second step.

We show in this paper that both integrated and differential Auger currents produced following absorption of a RCP photon in a rotating linear molecule are different from those which follow the absorption of a LCP photon. The reasons for the existence of this CD in AES (i.e., CDAES) are completely different from those for CDAD [2–7] of photoelectrons.

Absorption of a CP photon in the $E1$ approximation in a linear molecule is known to produce rotational orientation as well as alignment of the excited target or of its residual ion [see Eqs. (A8) or (I.A13) in Ref. [8], henceforth referred to as I]. But it is only the orientation which is affected by the helicity of the absorbed photon. Therefore, in order for CDAES to exist, it is necessary to include the effects of rotational orientation of a vacancy whose decay leads to the emission of an Auger electron. The integrated as well as differential cross sections for Auger emission have already been shown by us in Ref. [8] to depend, among other things, also on the rotational orientation of the decayed vacancy provided the ejected electron's spin is also observed. We will see in this paper that Auger electrons following absorption of a CP photon in a linear molecule are spin resolved even in the absence of SOI's and spin-rotation interactions (SRI's). Consequently, the dichroic effects produced by the absorption of circularly polarized (CP) light in a linear, gaseous molecule (which is neither polarized nor spatially fixed) can readily be probed by the spin-resolved AES. We will, in addition, show in this paper that CDAES is of the same order of magnitude as that of the total Auger intensity for unpolarized electrons and hence should readily be measurable experimentally.

In a CDAD experiment, on the other hand, one needs

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not observe the spins of photoelectrons. But a photoemission transition in this case is brought about by a vector operator in a polarized or spatially fixed molecule. Therefore the existence of CDAD requires simultaneous presence of two anisotropies: One in the form of a polarized or spatially fixed molecule, and the other due to nonisotropic interaction of the ionizing photon with the target. Moreover, unlike CDAES which is present in both integrated as well as differential Auger currents, the CD in photoelectron spectroscopy (PES) is observable only in angular photocurrent but vanishes in the integrated photoionization cross section from molecules [2,3(a),4–7]. (Cherepkov and Kuznetsov [3(b)] have, on the other hand, shown that CD may not be absent even in the integrated photocurrent if it is emitted in ionization of those polarized atoms which have a nonzero orientation factor.)

In this paper we develop a theory for studying CDAES following absorption of CP light in rotating linear molecules. In Sec. II we derive an expression for the angular distribution of spin-resolved Auger electrons in Hund's coupling scheme (b) [9,10]. Although we have used the parity-adapted [11] wave functions again for each of the molecular states involved in processes (1), however, unlike in our previous work [8], the effects of both SOI as well as of SRI in the second step of the decay of a vacancy resulting in the emission of an Auger electron have been neglected. Consequently, the expression for angle- and spin-resolved Auger-electron spectroscopy (ASRAES) arrived at by us in the next section is very different from that obtained in Eq. (I.21). An analysis of this expression along with that of the degree of polarization of Auger electrons is also presented in the following section.

In Sec. III, we specialize our ASRAES formulation to CDAES in rotating linear molecules. Its properties and its dependence on various parameters are discussed at length in that section. An application of the theories developed in this paper is presented in the subsequent section. Therein we show that when the absorption of a photon merely excites a molecule without ionizing it, i.e., for process (1a), the spin-resolved, integrated Auger current and its CD are proportional to the total Auger intensity for spin-undetected emission. The factors which specify the constant of proportionality are independent of all dynamics. The degree of spin polarization of this Auger current involves only these nondynamical factors and does not contain even the intensity term. It can therefore readily be calculated for any Auger transition taking place in a linear molecule via process (1a). The CD in the spin-resolved angular Auger current requires an additional parameter which, however, depends upon the Auger decay dynamics.

Section V describes the conclusion of our work.

II. THEORY FOR ASRAES

Let us consider ASRAES after absorption of a photon of frequency ν_γ in a rotating linear molecule AB in either of the two following possible ways:

$$h\nu_\gamma + AB(J_0M_0p_0) \rightarrow AB^*(JMp) \rightarrow AB^+(J_fM_fp_f) + e_A(\mathbf{k}_A, \hat{\mathbf{u}}_A\mu_A) \tag{1a}$$

or

$$h\nu_\gamma + AB(J_0M_0p_0) \rightarrow AB^{+*}(JMp) + e_p \tag{1b}$$

followed by

$$AB^{+*}(JMp) \rightarrow AB^{2+}(J_fM_fp_f) + e_A(\mathbf{k}_A, \hat{\mathbf{u}}_A\mu_A) \; . \tag{1c}$$

Here, e_A is the observed Auger electron of energy $\varepsilon_A = \hbar^2 k_A^2/2m_e$ ejected along $\mathbf{k}_A(k_A, \theta_A, \phi_A)$, with the spin projection $\mu_A\hbar$ in the quantization direction $\hat{\mathbf{u}}_A$ (θ'_A, ϕ'_A). [The e_p in (1b) stands for the unobserved photoelectron.] Both of the vectors $\mathbf{k}_A$ and $\hat{\mathbf{u}}_A$ are referred to the photon- (or laboratory, fixed frame of reference with its polar axis taken to be the direction of incidence of the unpolarized (UP) or CP electromagnetic radiation. If the incident beam is, however, plane polarized (PP), then its electric vector defines the polar axis of the photon frame.

The states of the molecules AB, AB^* (or AB^{+*}), and AB^+ (or AB^{2+}) participating in process (1a) [or (1b) and 1(c)] are represented, respectively, by $|J_0M_0p_0\rangle$, $|JMp\rangle$, and $|J_fM_fp_f\rangle$. Here, $(M_0\hbar, M\hbar, M_f\hbar)$ are the projections along the polar axis of the total angular momenta $(\mathbf{J}_0\hbar, \mathbf{J}\hbar, \mathbf{J}_f\hbar)$ of the three molecular states of parities (p_0, p, p_f) being considered in (1). We have represented the photoabsorption step in (1) either by the density matrix $\rho_{\text{ph}}(JMM'; 1m_\gamma)$ or by the state multiples $\langle [T(J; m_\gamma)]^\dagger_{KQ} \rangle$ related to each other by Eq. (I.3) derived by Blum [12]. The parameter m_γ ($=0, +1, -1$ for PP, RCP, and LCP, respectively) represents the nature of polarization of the incident light absorbed in the $E1$ approximation.

In the present paper, we are interested in investigating the angular distribution of spin-resolved Auger electrons e_A emitted in (1) in the absence of both the SOI and SRI in the final molecular state $|J_fM_fp_f\rangle$ of AB^+ (or AB^{2+}). Hund's coupling scheme (b) is based on the approximation that the SOI is weak compared to SRI [9,10]. Consequently, the electronic spin angular momentum $\mathbf{S}_f$ of AB^+ (or AB^{2+}) in this scheme is coupled to the sum $\mathbf{N}_f$ of the electronic orbital and nuclear rotational angular momenta to give the total angular momentum $\mathbf{J}_f = \mathbf{N}_f + \mathbf{S}_f$. Thus the J_f splitting of the energy levels of AB^+ in (1a) [or of AB^{2+} in (1c)] arises due to the SRI in Hund's case (b). In the limit when SRI is also weak, this fine-structure splitting of the energy levels will not be resolved. Therefore, in order to neglect the effects of both SOI as well as SRI in the coupling scheme (b), one should include a summation over J_f in the theory.

Hence the angular distribution of Auger electrons emitted in either of the processes (1) and spin resolved even in the absence of SOI and SRI in the final state $|J_fM_fp_f\rangle$ is given by

$$\frac{d\sigma_A(m_\gamma;\hat{\mathbf{u}}_A\mu_A)}{d\hat{\mathbf{k}}_A}=K_A\sum_{M,M',J_f,M_f}\rho_{\mathrm{ph}}(JMM';1m_\gamma)\langle J_fM_fp_f;\mathbf{k}_A\hat{\mathbf{u}}_A\mu_A|F_A|JMp\rangle\langle J_fM_fp_f;\mathbf{k}_A\hat{\mathbf{u}}_A\mu_A|F_A|JM'p\rangle^* \ . \tag{2}$$

This expression differs from that given in Eq. (I.2) by an extra sum over J_f present herein due to the above-explained reasons. Apart from this, K_A is again a constant but with a value different from that obtained from I; $\langle J_fM_fp_f;\mathbf{k}_A\hat{\mathbf{u}}_A\mu_A|F_A|JMp\rangle$ is the matrix element of the Auger transition operator F_A between the bra and ket states of AB^++e_A (or $AB^{2+}+e_A$) and AB^* (or AB^{+*}), respectively.

The sums over M, M', and M_f have already been carried out by us analytically in paper I and expression (2), without sum over J_f, shown to reduce to Eq. (I.18). On substituting (I.18), (I.12), and (I.17) from I into (2), one gets the following sum over j, j', and J_f which can readily be evaluated using an identity of the Racah algebra from Ref. [13]:

$$\sum_{j,j',J_f}(-1)^{j+J_f}(2j+1)(2j'+1)(2J_f+1)\begin{Bmatrix} j & j' & K \\ J & J & J_f \end{Bmatrix}\begin{Bmatrix} l & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ L & S_A & K \end{Bmatrix}\begin{Bmatrix} N_f & S_f & J_f \\ N & S & J \\ l & \frac{1}{2} & j \end{Bmatrix}\begin{Bmatrix} N_f & S_f & J_f \\ N & S & J \\ l' & \frac{1}{2} & j' \end{Bmatrix}$$

$$=(-1)^{1/2+l+N+S-J+N_f+S_f}\begin{Bmatrix} N & N & L \\ l & l' & N_f \end{Bmatrix}\begin{Bmatrix} S & S & S_A \\ \frac{1}{2} & \frac{1}{2} & S_f \end{Bmatrix}\begin{Bmatrix} N & S & J \\ N & S & J \\ L & S_A & K \end{Bmatrix} \ . \tag{3}$$

Expression (2) can subsequently be written as

$$\frac{d\sigma_A(m_\gamma;\hat{\mathbf{u}}_A\mu_A)}{d\hat{\mathbf{k}}_A}=\frac{\sigma_A}{A}\sum_{\substack{K,Q,\\ l,l'}}\rho_{KQ}(J;m_\gamma)G_A(NSJ;N_fS_f;KQ;ll';\hat{\mathbf{k}}_A\hat{\mathbf{u}}_A\mu_A)A_l(n_fN_f\Lambda_fp_f;nN\Lambda p)$$

$$\times A_{l'}^*(n_fN_f\Lambda_fp_f;nN\Lambda p) \ . \tag{4}$$

In this expression,

$$\sigma_A=K_A[(2N_f+1)\sqrt{2J+1}\langle[T(J;m_\gamma)]_{00}^\dagger\rangle A] \tag{5a}$$

is the total Auger intensity with

$$A=\sum_l(2l+1)^{-1}|A_l(n_fN_f\Lambda_fp_f;nN\Lambda p)|^2 \tag{5b}$$

and the Auger decay matrix element

$$A_l(n_fN_f\Lambda_fp_f;nN\Lambda p)=\tfrac{1}{2}(-i)^le^{i\sigma_l}\sqrt{2l+1}[1+(-1)^{l+N+N_f+p+p_f}]$$

$$\times\sum_m(-1)^m\left[\begin{bmatrix} N_f & l & N \\ -\Lambda_f & -m & \Lambda \end{bmatrix}\langle n_f\Lambda_f;lm|V_c|n\Lambda\rangle\right.$$

$$\left.+(-1)^p\begin{bmatrix} N_f & l & N \\ -\Lambda_f & -m & -\Lambda \end{bmatrix}\langle n_f\Lambda_f;lm|V_c|n-\Lambda\rangle\right] \ . \tag{5c}$$

The Coulomb amplitudes $\langle n_f\Lambda_f;lm|V_c|n\pm\Lambda\rangle$ have been defined in I. The geometrical factor present in (4) is given by

$$G_A(NSJ;N_fS_f;KQ;ll';\hat{\mathbf{k}}_A\hat{\mathbf{u}}_A\mu_A)=(-1)^{1+\mu_A+N+S+N_f+S_f+K+Q}(2N+1)(2S+1)\sqrt{2K+1}$$

$$\times\sum_{\substack{L,M_L,\\ S_A,M_A}}\sqrt{(2L+1)(2S_A+1)}\begin{bmatrix} l & l' & L \\ 0 & 0 & 0 \end{bmatrix}\begin{bmatrix} \frac{1}{2} & \frac{1}{2} & S_A \\ -\mu_A & \mu_A & 0 \end{bmatrix}\begin{bmatrix} L & S_A & K \\ M_L & M_A & -Q \end{bmatrix}$$

$$\times\begin{Bmatrix} N & N & L \\ l & l' & N_f \end{Bmatrix}\begin{Bmatrix} S & S & S_A \\ \frac{1}{2} & \frac{1}{2} & S_f \end{Bmatrix}\begin{Bmatrix} N & N & L \\ S & S & S_A \\ J & J & K \end{Bmatrix}Y_L^{M_L}(\hat{\mathbf{k}}_A)Y_{S_A}^{M_A}(\hat{\mathbf{u}}_A) \ . \tag{6}$$

We have thus been able to describe ASRAES even in the present case by an expression (4) which in form is identical to Eq. (I.18). But the dynamical [Eqs. (5)] and the geometrical [Eq. (6)] factors to be used in (4) are very different from the respective expressions (I.17) and (I.12) derived earlier [8]. The reason for this difference is that we have now neglected both the SOI and SRI for the final state $|J_f M_f p_f\rangle$ in Hund's coupling scheme (b). However, still the same rotational orientation and alignment factors ρ_{KQ} are to be used in the two papers. These are defined in Eq. (I.13). We have already derived in Appendixes A and B to paper I the expressions in Hund's coupling schemes (a) and (b), respectively, for the photoabsorption step involved in process (1b). In Appendix A to the present paper, on the other hand, we have found in both coupling schemes the ρ_{KQ} when the incident photon merely excites the molecule AB without ionizing it, i.e., for process (1a).

The selection rule, $l+N+N_f+p+p_f=\text{even}$, applicable to the Auger decay matrix element (5c) is, of course, identical to (I.10′) derived in Hund's coupling scheme (b). Thus, in the present case as well, either even or odd values of the partial wave l, needed to describe the Auger electron, will only contribute to (4). This separation of the Auger spectrum into even and odd partial waves will depend upon the values N, N_f, p, and p_f. The first 6-j symbol present in the geometrical factor (6) confines each of l and l' to be between $|N-N_f| \le l, l' \le N+N_f$. This condition is very different from that arrived at in I where both l and l' were found to be restricted by an inequality [8] which involved the total angular momentum J_f of AB^+ (or AB^{2+}). Therefore the use of parity-adapted molecular states for AB^* and AB^+ (or, AB^{+*} and AB^{2+}), in the calculation of the matrix elements (5c) not only divides the Auger spectrum into gerade (even l) and ungerade (odd l) parts, but also truncates the partial waves, needed to represent the continuum orbital of the Auger electron, from an infinite to a finite number. It happens in both Hund's coupling schemes (a) and (b) and irrespective of whether or not the J_f splitting of the energy levels of AB^+ (or AB^{2+}) is taken into account.

For the first 3-j symbol in (6) not to vanish identically, $l+l'+L$ must always be even. Since l and l' have the same parities, the L in (6) must be even as well. Now keeping in mind that in (6), $K=0$–2 always for an $E1$ process [see Eqs. (I.A13′) in I and (A8)] and $S=0$ and 1, the permitted values of L then become 0 and 2. One can, consequently, simplify (4) to the form

$$\frac{d\sigma_A(m_\gamma;\hat{\mathbf{u}}_A\mu_A)}{d\hat{\mathbf{k}}_A}=\frac{\sigma_A}{8\pi}\{1+\beta_A\rho_{20}(J;m_\gamma)P_2(\cos\theta_A)-2\mu_A\gamma_A\rho_{10}(J;m_\gamma)\cos\theta'_A$$
$$+\mu_A\delta_A\rho_{10}(J;m_\gamma)[(3\cos^2\theta_A-1)\cos\theta'_A+\tfrac{3}{2}\sin2\theta_A\sin\theta'_A\cos(\phi_A-\phi'_A)]\}\ . \tag{7}$$

Here

$$\beta_A=(-1)^{S+J+N_f}\frac{\sqrt{5}}{A}(2N+1)\sum_{l,l'}\begin{bmatrix} l & l' & 2\\ 0 & 0 & 0\end{bmatrix}\begin{Bmatrix} l & l' & 2\\ N & N & N_f\end{Bmatrix}\begin{Bmatrix} J & J & 2\\ N & N & S\end{Bmatrix}$$
$$\times A_l(n_fN_f\Lambda_fp_f;nN\Lambda p)A^*_{l'}(n_fN_f\Lambda_fp_f;nN\Lambda p)\ , \tag{8a}$$

$$\gamma_A=(-1)^{-1/2+N-J+S_f}\sqrt{2}(2S+1)\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1\\ S & S & S_f\end{Bmatrix}\begin{Bmatrix} J & J & 1\\ S & S & N\end{Bmatrix}, \tag{8b}$$

and

$$\delta_A=(-1)^{1/2+S+N+S_f+N_f}2\sqrt{15}(2N+1)(2S+1)A^{-1}\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1\\ S & S & S_f\end{Bmatrix}\begin{Bmatrix} N & S & J\\ N & S & J\\ 2 & 1 & 1\end{Bmatrix}$$
$$\times\sum_{l,l'}\begin{bmatrix} l & l' & 2\\ 0 & 0 & 0\end{bmatrix}\begin{Bmatrix} l & l' & 2\\ N & N & N_f\end{Bmatrix}A_l(n_fN_f\Lambda_fp_f;nN\Lambda p)A^*_{l'}(n_fN_f\Lambda_fp_f;nN\Lambda p)\ . \tag{8c}$$

The set of Eqs. (4)–(8) constitutes the first main result of this paper. Although expression (4) is applicable to any experimental arrangement, relations (7) and (8) have been derived for the most commonly used experimental geometry containing axial symmetry, with respect to the polar axis of the photon frame, i.e., taking $Q=0$ in (4).

Thus only four $(\sigma_A,\beta_A,\gamma_A,\delta_A)$, not the five $(\sigma_A,\beta_A,\gamma_A,\delta_A,\xi_A)$ present in (I.21), parameters are sufficient to describe ASRAES following photoabsorption in a rotating linear molecule in the absence of SRI in the final state $|J_fM_fp_f\rangle$ in Hund's coupling scheme (b). Although the polarization factors [i.e., $\rho_{10}(J;m_\gamma)$ and $\rho_{20}(J;m_\gamma)$] and the harmonic functions of the angles $\hat{\mathbf{k}}_A(\theta_A,\phi_A)$ and $\hat{\mathbf{u}}_A(\theta'_A,\phi'_A)$ associated with $(\sigma_A,\beta_A,\gamma_A,\delta_A)$ in (7) are identical to those present in (I.21), there is a big difference between the expressions

[(5a), (8a)–(8c) and (I.17′), (I.22a)–(I.22c)] in I for the four parameters. For example, γ_A in (8b) is totally independent of the Auger dynamics and is completely determined by the quantum numbers N,S,J (with $\mathbf{J}=\mathbf{N}+\mathbf{S}$) for the molecule AB^* (or AB^{+*}) and by the spin S_f of the ion AB^+ (or AB^{2+}) left after Auger emission.

The spin-resolved, integrated Auger current

$$\sigma_A(m_\gamma;\hat{\mathbf{u}}_A\mu_A)=\tfrac{1}{2}\sigma_A[1-2\mu_A\gamma_A\rho_{10}J;m_\gamma)\cos\theta'_A] \tag{9a}$$

and its degree of polarization

$$p(m_\gamma;\hat{\mathbf{u}}_A)=-\gamma_A\rho_{10}(J;m_\gamma)\cos\theta'_A \tag{9b}$$

are described by the equations identical to (I.24) and (I.25), respectively. The degree of spin polarization of the angular current is, on the other hand, given by

$$p(m_\gamma;\hat{\mathbf{u}}_A\hat{\mathbf{k}}_A)=\mathbf{p}\cdot\hat{\mathbf{u}}_A, \tag{10a}$$

where

$$\frac{d\sigma_A(m_\gamma)}{d\hat{\mathbf{k}}_A}p_x=\frac{3\sigma_A}{16\pi}\delta_A\rho_{10}(J;m_\gamma)\sin(2\theta_A)\cos\phi_A\ , \tag{10b}$$

$$\frac{d\sigma_A(m_\gamma)}{d\hat{\mathbf{k}}_A}p_y=\frac{3\sigma_A}{16\pi}\delta_A\rho_{10}(J;m_\gamma)\sin(2\theta_A)\sin\phi_A\ , \tag{10c}$$

and

$$\frac{d\sigma_A(m_\gamma)}{d\hat{\mathbf{k}}_A}p_z=\frac{\sigma_A}{8\pi}[(3\cos^2\theta_A-1)\delta_A-2\gamma_A]\rho_{10}(J;m_\gamma) \tag{10d}$$

are the three Cartesian components of the polarization vector $\mathbf{p}$ with

$$\frac{d\sigma_A(m_\gamma)}{d\hat{\mathbf{k}}_A}=\frac{\sigma_A}{4\pi}[1+\beta_A\rho_{20}(J;m_\gamma)P_2(\cos\theta_A)] \tag{11}$$

the angular distribution of spin-undetected Auger electrons. The expressions (10b)–(10d) can be obtained either directly from (7) or by substituting $\xi_A=0$ in (I.27a)–(I.27c) in I.

It is obvious from Eqs. (9b) and (10b)–(10d) that for the Auger electrons to have a nonzero degree of spin polarization they should be emitted in the decay of a rotationally oriented vacancy. We have shown in the two appendixes in Ref. [8] and also in Appendix A to this paper that for $\rho_{10}(J;m_\gamma)$ not to vanish identically in both Hund's coupling schemes (a) and (b), the photons absorbed in processes (1) should be CP. Klar [14], Huang [15], and Blum, Lohmann, and Taute [16] have called this mechanism "polarization transfer" in the context of Auger electrons emitted in the decay of an atomic vacancy.

Furthermore, the second 6-j symbol in (8a) means that for β_A not to vanish identically, we must have $J\geq 1$. That is, only those spin-unresolved, molecular Auger electrons will have a nonisotropic distribution (11) which are emitted in the decay of a rotationally aligned vacancy with $J\geq 1$. It is also obvious from (8b) and 8(c) that both γ_A and δ_A will be trivially zero if $S<\frac{1}{2}$ or $J<\frac{1}{2}$. Thus if we want the Auger electrons e_A emitted in (1) to be spin resolved, then AB^* (or AB^{+*}) should be in an electronic state other than singlet with its total angular momentum $J\geq\frac{1}{2}$.

III. CIRCULAR DICHROISM IN AUGER SPECTROSCOPY

The CD in ASRAES is defined by

$$\frac{d\sigma_A^{\mathrm{CD}}(\hat{\mathbf{u}}_A\mu_A)}{d\hat{\mathbf{k}}_A}\equiv\frac{d\sigma_A(m_\gamma=+1;\hat{\mathbf{u}}_A\mu_A)}{d\hat{\mathbf{k}}_A}-\frac{d\sigma_A(m_\gamma=-1;\hat{\mathbf{u}}_A\mu_A)}{d\hat{\mathbf{k}}_A}\ . \tag{12}$$

On substituting (7) and using the properties $\rho_{20}(J;+1)=\rho_{20}(J;-1)$ and $\rho_{10}(J;+1)=-\rho_{10}(J;-1)$ either from Eq. (I.A13′) or from (A8), we find

$$\frac{d\sigma_A^{\mathrm{CD}}(\hat{\mathbf{u}}_A\mu_A)}{d\hat{\mathbf{k}}_A}=\frac{\sigma_A}{4\pi}\mu_A\{2\gamma_A\cos\theta'_A-\delta_A[(3\cos^2\theta_A-1)\cos\theta'_A+\tfrac{3}{2}\sin(2\theta_A)\sin\theta'_A\cos(\phi_A-\phi'_A)]\}\rho_{10}(J;-1)\ . \tag{13}$$

Similarly, CD in the spin-resolved, integrated Auger current, i.e.,

$$\sigma_A^{\mathrm{CD}}(\hat{\mathbf{u}}_A\mu_A)=2\mu_A\gamma_A\rho_{10}(J;-1)\sigma_A\cos\theta'_A\ , \tag{14}$$

is obtained from (9a). Expressions (13) and (14), which are the second main results of this paper, give us CDAES. In the following, we discuss their important properties which are applicable to rotating linear molecules belonging to either of the $C_{\infty v}$ or $D_{\infty h}$ groups

(i) It is obvious from the respective Eqs. (13) and (14) that

$$\frac{d\sigma_A^{\mathrm{CD}}}{d\hat{\mathbf{k}}_A}=\sum_{\mu_A}\frac{d\sigma_A^{\mathrm{CD}}(\hat{\mathbf{u}}_A\mu_A)}{d\hat{\mathbf{k}}_A}=0\ ,$$

$$\sigma_A^{\mathrm{CD}}\equiv\sum_{\mu}\sigma_A^{\mathrm{CD}}(\hat{\mathbf{u}}_A\mu_A)=0\ .$$

Thus CDAES vanishes identically for Auger electrons observed without their spins.

(ii) According to Eq. (14), CD may be present also in the integrated Auger current from rotationally polarized linear molecules. σ_A^{CD} will necessarily vanish for those

Auger electrons which are polarized in the x-y plane of the photon frame, i.e., perpendicular $(\theta'_A=\pi/2)$ to the direction of incidence of the CP radiation absorbed in (1).

(iii) Unlike CDAD of photoelectrons, the $d\sigma_A^{\rm CD}(\hat{\mathbf{u}}_A\mu_A)/d\hat{\mathbf{k}}$ does not necessarily vanish even for a coplanar experimental arrangement, i.e., when the incident photon beam, outgoing Auger electron, and their spin-quantization axis are in the same plane (i.e., $\phi_A=\phi'_A$).

(iv) The CDAES (13) will necessarily be zero for Auger electrons emitted in the forward $(\theta_A=0)$ or backward $(\theta_A=\pi)$ directions and polarized transversely to their direction of propagation (i.e., $\theta'_A=\pi/2$). $d\sigma_A^{\rm CD}(\hat{\mathbf{u}}_A\mu_A)/d\hat{\mathbf{k}}_A$ will vanish also for longitudinally polarized Auger electrons moving in the x-y plane (i.e., $\theta_A,\theta'_A=\pi/2$).

(v) The rotational orientation produced by the absorption of CP light in a liner molecule can be completely and directly probed by measuring CDAES in any directions other than those mentioned in (ii) and (iv) where it vanishes identically.

(vi) It is obvious from Eqs. (8b), (8c), (13), and (14) that CDAES may exist only for those Auger electrons which are emitted from a nonsinglet electronic state of AB^* (or AB^{+*}) with total angular momentum $J\geq\frac{1}{2}$.

The relations (13) and (14) can be combined into a single expression of the form

$$\frac{d\sigma_A^{\rm CD}(\hat{\mathbf{u}}_A\mu_A)}{d\hat{\mathbf{k}}_A}=\frac{\sigma_A^{\rm CD}(\hat{\mathbf{u}}_A\mu_A)}{4\pi}\left\{1-\tfrac{1}{2}[3\cos^2\theta_A-1)+\tfrac{3}{2}\sin(2\theta_A)\tan\theta'_A\cos(\phi_A-\phi'_A)]\frac{\delta_A}{\gamma_A}\right\}. \tag{15}$$

Thus the whole of CDAES is completely specified by just two quantities: Namely, the $\sigma_A^{\rm CD}(\hat{\mathbf{u}}_A\mu_A)$ in the spin-resolved integrated Auger current and the ratio of parameters δ_A to γ_A. The former is given by Eq. (14), whereas the latter is obtained from (8b) and (8c).

Let us consider the following three simple experimental arrangements to measure $d\sigma_A^{\rm CD}(\hat{\mathbf{u}}_A\mu_A)/d\hat{\mathbf{k}}_A$.

(a) $\theta_A=\theta'_A$ and $\phi_A=\phi'_A$. That is, $\hat{\mathbf{u}}_A$ is parallel to $\hat{\mathbf{k}}_A$ and the Auger electrons are longitudinally polarized. Then (15) becomes

$$\frac{d\sigma_A^{\rm CD}(\hat{\mathbf{u}}_{\rm long}\mu_A)}{d\hat{\mathbf{k}}_A}=\frac{1}{4\pi}\left[1-\frac{\delta_A}{\gamma_A}\right]\sigma_A^{\rm CD}(\hat{\mathbf{u}}_{\rm long}\hat{\mu}_A). \tag{16a}$$

(b) $\theta'_A=\theta_A+\pi/2$ and $\phi'_A=\phi_A$ for $0\leq\theta_A\leq\pi/2$, or $\theta'_A=\theta_A-3\pi/2$ and $\phi'_A=\phi_A+\pi$ for $\pi/2\leq\theta_A\leq\pi$. That is, $\hat{\mathbf{u}}_A$ is parallel to the (say, scattering) plane which contains Auger electrons plus the incident beam of CP radiation, and the Auger electrons are polarized transversely to their direction of propagation We now obtain

$$\frac{d\sigma_A^{\rm CD}(\hat{\mathbf{u}}_{\parallel\rm trans}\hat{\mu}_A)}{d\hat{\mathbf{k}}_A}=\frac{1}{4\pi}\left[1+\frac{1}{2}\frac{\delta_A}{\gamma_A}\right]\sigma_A^{\rm CD}(\hat{\mathbf{u}}_{\parallel\rm trans}\mu_A). \tag{16b}$$

(c) $\theta'_A=\pi/2$ and $\phi'_A=\phi_A+\pi/2$. That is, $\hat{\mathbf{u}}_A$ is perpendicular to the scattering plane and the Auger electrons are transversely polarized. In this case, both

$$\frac{d\sigma_A^{\rm CD}(\hat{\mathbf{u}}_{\perp\rm trans}\mu_A)}{d\hat{\mathbf{k}}_A}=0 \tag{16c}$$

and

$$\sigma_A^{\rm CD}(\hat{\mathbf{u}}_{\perp\rm trans}\mu_A)=0. \tag{16d}$$

Thus the ratio of the CD in the differential Auger cross section to that in the integrated Auger current for spin-resolved emission is just a constant for the experimental arrangements (16a) and (16b). The measurement of this ratio for either experimental geometry will directly give us δ_A/γ_A. But γ_A in (8b) is completely determined by the quantum numbers N,S,J for AB^* (or AB^{+*}) and S_f for AB^+ (or AB^{2+}). Therefore, once δ_A/γ_A is measured from (16a) and (16b), one can readily find δ_A which, however, depends on the Auger dynamics in (8c). A knowledge of $\sigma_A^{\rm CD}(\hat{\mathbf{u}}_A\mu_A)$ will, on the other hand, give the value of the rotational orientation factor $\rho_{10}(J;-1)$ from (14).

In order to specify the angular distribution (7) of spin-resolved Auger electrons, one needs to know, in addition, the parameter β_A and the rotational alignment factor $\rho_{20}(J;m_\gamma)$. Both of these can be readily extracted from measurements on the angular distribution (11) for spin-unresolved Auger electrons.

IV. APPLICATION

In order to apply the theory developed in the last two sections and to see the order of magnitude of the values of various experimental observables discussed therein, let us consider emission of Auger electrons via process (1a) in a rotating linear molecule. In Appendix A we have shown that in this case the rotational orientation and alignment factors are totally independent of dynamical terms and are completely determined analytically by the expression (A8). Equations (8b) and (A8) give

$$\gamma_A\rho_{10}(J;m_\gamma)=(-1)^{-1/2+J_0+N+S_f}3(2S+1)m_\gamma \times\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & 1\\ S & S & S_f\end{Bmatrix}\begin{Bmatrix}J & J & 1\\ S & S & N\end{Bmatrix}\begin{Bmatrix}1 & 1 & 1\\ J & J & J_0\end{Bmatrix}. \tag{17}$$

Thus, once (17) is calculated for given values of the quantum number J_0 for AB, (N,S,J) for AB^*, and S_f for AB^+, one can readily find the spin-resolved integrated Auger cross section $\sigma_A(m_\gamma;\hat{\mathbf{u}}_A\mu_A)$ from (9a), its degree of polarization $p(m_\gamma;\hat{\mathbf{u}}_A)$ from (9b), and also the corresponding dichroism $\sigma_A^{\rm CD}(\hat{\mathbf{u}}_A\mu_A)$ from (14).

It is interesting to see that the product (17) contains neither of the quantum numbers N_0 and S_0 which specify, respectively, the rotational state and spin of the molecule AB. This, in turn, means that none of the three observables $\sigma_A(m_\gamma;\hat{\mathbf{u}}_A\mu_A)$, $P(m_\gamma;\hat{\mathbf{u}}_A)$, and $\sigma_A^{\rm CD}(\hat{\mathbf{u}}_A\mu_A)$ for Auger electrons emitted via process (1a) will be affected by a change in the values of N_0 and S_0 as long as the total angular momentum $\mathbf{J}_0=\mathbf{N}_0+\mathbf{S}_0$ remains unchanged. In addition, only two $[\sigma_A(m_\gamma;\hat{\mathbf{u}}_A\mu_A)$ and $\sigma_A^{\rm CD}(\hat{\mathbf{u}}_A\mu_A)]$ of the three observables depend upon the rotational state of the residue AB^+ due to the presence of N_f in the total Auger intensity σ_A defined by Eqs. (5). The degree of spin polarization $P(m_\gamma;\hat{\mathbf{u}}_A)$ will be independent of N_f as well.

One readily finds from the first and the second 6-j symbols present in (17) that for this expression not to vanish identically, one must have $S\geq\frac{1}{2}$ for the spin of the photoexcited molecule AB^* whose decay leads to the emission of an Auger electron. The second and third 6-j symbols, on the other hand, impose the condition $J\geq\frac{1}{2}$ on the total angular momentum of AB^*. Similarly, we must also have $S_f=|S-\frac{1}{2}|$, $S+\frac{1}{2}$, and $J_0=|J-1|,J,J+1$ (with $J=0$ not permitted and J,J_0 should both either be integers or half integers) for the $\gamma_A\rho_{10}(J;m_\gamma)$ not to vanish trivially.

In Appendix B to this paper we have developed expressions for the product (17) in terms of N,S,J applicable to all permissible values of these quantum numbers and also of J_0,S_f. Table I contains calculated values of $\gamma_A\rho_{10}(J;m_\gamma)$ for $N=0-10$ with $S=\frac{1}{2},1$.

On multiplying the appropriate entry of this table by $-\cos\theta'_A$, one straight away obtains the degree of polarization (9b) of the integrated Auger current emitted in process (1a). If, on the other hand, we substitute the tabulated values of $\gamma_A\rho_{10}(J;m_\gamma)$ in Eqs. (9a) and (14), one gets spin-resolved, integrated Auger current and the corresponding CD, respectively. For example, for each of the three transitions $h\nu+AB(J_0=\frac{5}{2};\frac{1}{2};5)\rightarrow AB^*(N=1,\ S=\frac{1}{2},\ J=\frac{3}{2};\ 2,\ \frac{1}{2},\ \frac{3}{2};\ 3,1,4)\rightarrow AB^+(S_f=0;0;\frac{1}{2})$ specified by the (7th; 13th; 31st) row and (8th; 6th; 8th) column, respectively, we find that $\sigma_A(m_\gamma;\hat{\mathbf{u}}_A\mu_A)=\sigma_A[1-\frac{1}{4}m_\gamma\mu_A\cos\theta'_A]/2$, $P(m_\gamma;\hat{\mathbf{u}}_A)=-\frac{1}{8}m_\gamma\cos\theta'_A$, $\sigma_A^{\rm CD}(\hat{\mathbf{u}}_A,\mu_A)=-\frac{1}{4}\mu_A\sigma_A\cos\theta'_A$. Thus, while up to 12.5% of the emitted Auger electrons may be spin polarized, determination of cross section for these transitions as well as of the CD need the total Auger intensity σ_A. Hence, depending on the values of σ_A, both $\sigma_A(m_\gamma;\hat{\mathbf{u}}_A\mu_A)$ and $\sigma_A^{\rm CD}(\hat{\mathbf{u}}_A\mu_A)$ may be experimentally measurable even for those Auger transitions in (1a) which take place via higher rotational states of AB^* and have relatively smaller values of $\gamma_A\rho_{10}(J;m_\gamma)$ in Table I.

In order to calculate the spin-resolved differential Auger cross section (7), its degree of polarization (10), and the CD (13) one needs, in addition to γ_A and ρ_{10}, the parameters β_A, δ_A, and the alignment factor ρ_{20}. The last quantity is again readily obtained from Eq. (A8) for process (1a). but the calculations of both β_A and δ_A from Eqs. (8a) and (8c), respectively, will require a knowledge of the Auger decay matrix element (5c).

Let us consider a situation when β_A and δ_A too become independent of the dynamical terms. One such case occurs if the residual molecule AB^+ (or AB^{2+}) is left in its ground rotational state, i.e., $N_f=0$ after Auger emission. The 6-j symbol present in (8a) and (8c) will now be zero unless l and l' are equal to N. In view of (5b), one finds

$$\beta_A=(-1)^{S+J}\sqrt{5}(2N+1)\begin{pmatrix}N&N&2\\0&0&0\end{pmatrix}\begin{Bmatrix}N&N&2\\J&J&S\end{Bmatrix}\tag{18a}$$

and

$$\delta_A=(-1)^{1/2+N+S+S_f}2\sqrt{15}(2N+1)(2S+1)\times\begin{pmatrix}N&N&2\\0&0&0\end{pmatrix}\begin{Bmatrix}\frac{1}{2}&\frac{1}{2}&1\\S&S&S_f\end{Bmatrix}\begin{Bmatrix}N&N&2\\S&S&1\\J&J&1\end{Bmatrix}.\tag{18b}$$

That is, both β_A and δ_A become independent of the Auger decay matrix element originally present in the respective expressions (8a) and (8c). Consequently, (8b) and (18b) yield

$$\frac{\delta_A}{\gamma_A}=(-1)^{1+S+J}(2N+1)\sqrt{30}\begin{pmatrix}N&N&2\\0&0&0\end{pmatrix}\times\begin{Bmatrix}N&N&2\\S&S&1\\J&J&1\end{Bmatrix}\begin{Bmatrix}S&S&1\\J&J&N\end{Bmatrix}^{-1}.\tag{19}$$

These simple relations, along with (8b), can be used to calculate β_A, δ_A, and δ_A/γ_A for any value of the quantum numbers (N,S,J,S_f). These are applicable to electrons emitted via either of the processes (1).

Let us consider first two rotational states of AB^* (or AB^{+*}), i.e., $N=0$ and 1. That $\delta_A/\gamma_A=0$ for $N=0$ is obvious from (19). But for $N=1$ we, on the other hand, obtain, again from (19), that $\delta_A/\gamma_A=\frac{2}{5}$ and $\delta_A/\gamma_A=-2(2S^2+S+1)/[5(S^2+S+1)]$ for $J=S\pm1$ and S, respectively. Relations (16a) and (16b) now give

$$\begin{aligned}\frac{d\sigma_A^{\rm CD}(\hat{\boldsymbol{\mu}}_{\rm long}\mu_A)}{d\hat{\mathbf{k}}_A}&=\frac{1}{4\pi}\sigma_A^{\rm CD}(\hat{\mathbf{u}}_{\rm long}\mu_A)\,,\\ \frac{d\sigma_A^{\rm CD}(\hat{\mathbf{u}}_{\|{\rm trans}}\mu_A)}{d\hat{\mathbf{k}}_A}&=\frac{1}{4\pi}\sigma_A^{\rm CD}(\hat{\mathbf{u}}_{\|{\rm trans}}\mu_A)\end{aligned}\tag{20a}$$

for $N,N_f=0$ and

$$\begin{aligned}\frac{d\sigma_A^{\rm CD}(\hat{\mathbf{u}}_{\rm long}\mu_A)}{d\hat{\mathbf{k}}_A}&=\frac{3}{5}\frac{1}{4\pi}\sigma_A^{\rm CD}(\hat{\mathbf{u}}_{\rm long}\mu_A)\,,\\ \frac{d\sigma_A^{\rm CD}(\hat{\mathbf{u}}_{\|{\rm trans}}\mu_A)}{d\hat{\mathbf{k}}_A}&=\frac{6}{5}\frac{1}{4\pi}\sigma_A^{\rm CD}(\hat{\mathbf{u}}_{\|{\rm trans}}\mu_A)\end{aligned}\tag{20b}$$

for $N=1$, $N_f=0$, and $J=S\pm1$.

TABLE I. Values of $\gamma\,{}_{A}\rho_{10}(J;m_\gamma)$ calculated from Eqs. (B1)–(B9). Eleven rotational states ($N=0-10$) of AB^* in (1a), with spin $S=\frac{1}{2}$ and 1 ($S=0$ not allowed) are considered. The total angular momentum of this photoexcited molecule is given by $J=|N-S|$ to $N+S$ (with $J=0$ prohibited). The spin of the molecular ion AB^+ left after Auger emission is $S_f=|S-\frac{1}{2}|$ and $S+\frac{1}{2}$. The sixth, seventh, and eighth columns of this table contain $\gamma\,{}_{A}\rho_{01}(J;m_\gamma)$ for the total angular momentum J_0 of AB to be, respectively, $|J-1|$, J, and $J+1$. The entries of columns six, seven, and eight should be multiplied by m_γ ($=+1$ for RCP light, -1 for LCP light) before use.

State					$\gamma\,{}_{A}\rho_{10}(J;m_\gamma)$		
State number	N	S	J	S_f	$J_0=\|J-1\|$	$J_0=J$	$J_0=J+1$
1	0	$\frac{1}{2}$	$\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{4}$
2				1	$\frac{1}{6}$	$\frac{1}{6}$	$-\frac{1}{12}$
3		1	1	$\frac{1}{2}$	$-\frac{1}{3}$	$-\frac{1}{6}$	$\frac{1}{6}$
4				$\frac{3}{2}$	$\frac{1}{6}$	$\frac{1}{12}$	$-\frac{1}{12}$
5	1	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{6}$	$\frac{1}{6}$	$-\frac{1}{12}$
6				1	$-\frac{1}{18}$	$-\frac{1}{18}$	$\frac{1}{36}$
7			$\frac{3}{2}$	0	$-\frac{5}{24}$	$-\frac{1}{12}$	$\frac{1}{8}$
8				1	$\frac{5}{72}$	$\frac{1}{36}$	$-\frac{1}{24}$
9		1	1	$\frac{1}{2}$	$-\frac{1}{6}$	$-\frac{1}{12}$	$\frac{1}{12}$
10				$\frac{3}{2}$	$\frac{1}{12}$	$\frac{1}{24}$	$-\frac{1}{24}$
11			2	$\frac{1}{2}$	$-\frac{3}{20}$	$-\frac{1}{20}$	$\frac{1}{10}$
12				$\frac{3}{2}$	$\frac{3}{40}$	$\frac{1}{40}$	$-\frac{1}{20}$
13	2	$\frac{1}{2}$	$\frac{3}{2}$	0	$\frac{1}{8}$	$\frac{1}{20}$	$-\frac{3}{40}$
14				1	$-\frac{1}{24}$	$-\frac{1}{60}$	$\frac{1}{40}$
15			$\frac{5}{2}$	0	$-\frac{7}{60}$	$-\frac{1}{30}$	$\frac{1}{12}$
16				1	$\frac{7}{180}$	$\frac{1}{90}$	$-\frac{1}{36}$
17		1	1	$\frac{1}{2}$	$\frac{1}{6}$	$\frac{1}{12}$	$-\frac{1}{12}$
18				$\frac{3}{2}$	$-\frac{1}{12}$	$-\frac{1}{24}$	$\frac{1}{24}$
19			2	$\frac{1}{2}$	$-\frac{1}{20}$	$-\frac{1}{60}$	$\frac{1}{30}$
20				$\frac{3}{2}$	$\frac{1}{40}$	$\frac{1}{120}$	$-\frac{1}{60}$
21			3	$\frac{1}{2}$	$-\frac{2}{21}$	$-\frac{1}{42}$	$\frac{1}{14}$
22				$\frac{3}{2}$	$\frac{1}{21}$	$\frac{1}{84}$	$-\frac{1}{28}$
23	3	$\frac{1}{2}$	$\frac{5}{2}$	0	$\frac{1}{12}$	$\frac{1}{42}$	$-\frac{5}{84}$
24				1	$-\frac{1}{36}$	$-\frac{1}{126}$	$\frac{5}{126}$
25			$\frac{7}{2}$	0	$-\frac{9}{112}$	$-\frac{1}{56}$	$\frac{1}{16}$
26				1	$\frac{9}{336}$	$\frac{1}{168}$	$-\frac{1}{48}$
27		1	2	$\frac{1}{2}$	$\frac{1}{10}$	$\frac{1}{30}$	$-\frac{1}{15}$
28				$\frac{3}{2}$	$-\frac{1}{20}$	$-\frac{1}{60}$	$\frac{1}{30}$
29			3	$\frac{1}{2}$	$-\frac{1}{42}$	$-\frac{1}{48}$	$\frac{1}{56}$
30				$\frac{3}{2}$	$\frac{1}{84}$	$\frac{1}{336}$	$-\frac{1}{112}$
31			4	$\frac{1}{2}$	$-\frac{5}{72}$	$-\frac{1}{72}$	$\frac{1}{8}$
32				$\frac{3}{2}$	$\frac{5}{144}$	$\frac{1}{144}$	$-\frac{1}{36}$
33	4	$\frac{1}{2}$	$\frac{9}{2}$	0	$-\frac{11}{180}$	$-\frac{1}{90}$	$\frac{1}{20}$
34				1	$\frac{11}{540}$	$\frac{1}{270}$	$-\frac{1}{60}$
35			$\frac{7}{2}$	0	$\frac{1}{16}$	$\frac{1}{72}$	$-\frac{7}{144}$
36				1	$-\frac{1}{48}$	$-\frac{1}{216}$	$\frac{7}{432}$
37		1	5	$\frac{1}{2}$	$-\frac{3}{55}$	$-\frac{1}{110}$	$\frac{1}{22}$
38				$\frac{3}{2}$	$\frac{3}{110}$	$\frac{1}{220}$	$-\frac{1}{44}$
39			4	$\frac{1}{2}$	$-\frac{1}{72}$	$-\frac{1}{360}$	$\frac{1}{90}$
40				$\frac{3}{2}$	$\frac{1}{144}$	$\frac{1}{720}$	$-\frac{1}{180}$
41			3	$\frac{1}{2}$	$\frac{1}{14}$	$\frac{1}{56}$	$-\frac{3}{56}$
42				$\frac{3}{2}$	$-\frac{1}{28}$	$-\frac{1}{112}$	$\frac{3}{112}$
43	5	$\frac{1}{2}$	$\frac{11}{2}$	0	$-\frac{13}{264}$	$-\frac{1}{132}$	$\frac{1}{24}$
44				1	$\frac{13}{792}$	$\frac{1}{396}$	$-\frac{1}{72}$
45			$\frac{9}{2}$	0	$\frac{1}{20}$	$\frac{1}{110}$	$-\frac{9}{220}$
46				1	$-\frac{1}{60}$	$-\frac{1}{330}$	$\frac{9}{660}$

TABLE I. (*Continued*).

State					$\gamma_A\rho_{10}(J;m_\gamma)$		
number	N	S	J	S_f	$J_0=\|J-1\|$	$J_0=J$	$J_0=J+1$
47		1	6	$\frac{1}{2}$	$-\frac{7}{156}$	$-\frac{1}{156}$	$\frac{1}{26}$
48				$\frac{3}{2}$	$\frac{7}{312}$	$\frac{1}{312}$	$-\frac{1}{52}$
49			5	$\frac{1}{2}$	$-\frac{1}{110}$	$-\frac{1}{660}$	$\frac{1}{132}$
50				$\frac{3}{2}$	$\frac{1}{220}$	$\frac{1}{1320}$	$\frac{1}{264}$
51			4	$\frac{1}{2}$	$\frac{1}{18}$	$\frac{1}{90}$	$-\frac{2}{45}$
52				$\frac{3}{2}$	$-\frac{1}{36}$	$-\frac{1}{180}$	$\frac{1}{45}$
53	6	$\frac{1}{2}$	$\frac{13}{2}$	0	$-\frac{15}{364}$	$-\frac{1}{182}$	$\frac{1}{28}$
54				1	$\frac{15}{1092}$	$\frac{1}{546}$	$-\frac{1}{84}$
55			$\frac{11}{2}$	0	$\frac{1}{24}$	$\frac{1}{156}$	$-\frac{11}{312}$
56				1	$-\frac{1}{72}$	$-\frac{1}{468}$	$\frac{11}{936}$
57		1	7	$\frac{1}{2}$	$-\frac{4}{105}$	$-\frac{1}{210}$	$\frac{1}{30}$
58				$\frac{3}{2}$	$\frac{2}{205}$	$\frac{1}{420}$	$-\frac{1}{60}$
59			6	$\frac{1}{2}$	$-\frac{1}{156}$	$-\frac{1}{1092}$	$\frac{1}{182}$
60				$\frac{3}{2}$	$\frac{1}{312}$	$\frac{1}{2184}$	$-\frac{1}{364}$
61			5	$\frac{1}{2}$	$\frac{1}{22}$	$\frac{1}{132}$	$-\frac{5}{132}$
62				$\frac{3}{2}$	$-\frac{1}{44}$	$-\frac{1}{264}$	$\frac{5}{264}$
63	7	$\frac{1}{2}$	$\frac{15}{2}$	0	$-\frac{17}{480}$	$-\frac{1}{240}$	$\frac{1}{32}$
64				1	$\frac{17}{1440}$	$\frac{1}{720}$	$-\frac{1}{96}$
65			$\frac{13}{2}$	0	$\frac{1}{28}$	$\frac{1}{210}$	$-\frac{13}{420}$
66				1	$-\frac{1}{84}$	$-\frac{1}{630}$	$\frac{13}{1260}$
67		1	8	$\frac{1}{2}$	$-\frac{9}{272}$	$-\frac{1}{272}$	$\frac{1}{34}$
68				$\frac{3}{2}$	$\frac{9}{544}$	$\frac{1}{544}$	$-\frac{1}{68}$
69			7	$\frac{1}{2}$	$-\frac{1}{210}$	$-\frac{1}{1600}$	$\frac{1}{240}$
70				$\frac{3}{2}$	$\frac{1}{420}$	$\frac{1}{3360}$	$-\frac{1}{480}$
71			6	$\frac{1}{2}$	$\frac{1}{26}$	$\frac{1}{182}$	$-\frac{3}{91}$
72				$\frac{3}{2}$	$-\frac{1}{52}$	$-\frac{1}{364}$	$\frac{3}{182}$
73	8	$\frac{1}{2}$	$\frac{17}{2}$	0	$-\frac{19}{612}$	$-\frac{1}{306}$	$\frac{1}{36}$
74				1	$\frac{19}{1836}$	$\frac{1}{918}$	$-\frac{1}{108}$
75			$\frac{15}{2}$	0	$\frac{1}{32}$	$\frac{1}{272}$	$-\frac{15}{544}$
76				1	$-\frac{1}{96}$	$-\frac{1}{816}$	$\frac{15}{1632}$
77		1	9	$\frac{1}{2}$	$-\frac{5}{171}$	$-\frac{1}{342}$	$\frac{1}{38}$
78				$\frac{3}{2}$	$\frac{5}{342}$	$\frac{1}{684}$	$-\frac{1}{76}$
79			8	$\frac{1}{2}$	$-\frac{1}{272}$	$-\frac{1}{2448}$	$\frac{1}{306}$
80				$\frac{3}{2}$	$\frac{1}{544}$	$\frac{1}{4896}$	$-\frac{1}{612}$
81			7	$\frac{1}{2}$	$\frac{1}{30}$	$\frac{1}{240}$	$-\frac{7}{240}$
82				$\frac{3}{2}$	$-\frac{1}{60}$	$-\frac{1}{480}$	$\frac{7}{480}$
83	9	$\frac{1}{2}$	$\frac{19}{2}$	0	$-\frac{21}{760}$	$-\frac{1}{380}$	$\frac{1}{40}$
84				1	$\frac{19}{1836}$	$\frac{1}{1140}$	$-\frac{1}{120}$
85			$\frac{17}{2}$	0	$\frac{1}{36}$	$\frac{1}{342}$	$-\frac{17}{684}$
86				1	$-\frac{1}{108}$	$-\frac{1}{1026}$	$\frac{17}{2052}$
87		1	10	$\frac{1}{2}$	$-\frac{11}{420}$	$-\frac{1}{420}$	$\frac{1}{42}$
88				$\frac{3}{2}$	$\frac{11}{840}$	$\frac{1}{840}$	$-\frac{1}{84}$
89			9	$\frac{1}{2}$	$-\frac{1}{342}$	$-\frac{1}{3420}$	$\frac{1}{380}$
90				$\frac{3}{2}$	$\frac{1}{684}$	$\frac{1}{6840}$	$-\frac{1}{760}$
91			8	$\frac{1}{2}$	$\frac{1}{34}$	$\frac{1}{306}$	$-\frac{4}{153}$
92				$\frac{3}{2}$	$-\frac{1}{68}$	$-\frac{1}{612}$	$\frac{2}{153}$
93	10	$\frac{1}{2}$	$\frac{21}{2}$	0	$-\frac{23}{924}$	$-\frac{1}{462}$	$\frac{1}{44}$
94				1	$\frac{21}{2280}$	$\frac{1}{1386}$	$-\frac{1}{132}$
95			$\frac{19}{2}$	0	$\frac{1}{40}$	$\frac{1}{420}$	$-\frac{19}{840}$
96				1	$-\frac{1}{120}$	$-\frac{1}{1260}$	$\frac{19}{2520}$

TABLE I. (*Continued*).

State number	N	S	J	S_f	$\gamma_A\rho_{10}(J;m_\gamma)$ $J_0=\|J-1\|$	$J_0=J$	$J_0=J+1$
97		1	11	$\frac{1}{2}$	$-\frac{6}{253}$	$-\frac{1}{506}$	$\frac{1}{46}$
98				$\frac{3}{2}$	$\frac{3}{253}$	$\frac{1}{1012}$	$-\frac{1}{92}$
99			10	$\frac{1}{2}$	$-\frac{1}{420}$	$-\frac{1}{4620}$	$\frac{1}{462}$
100				$\frac{3}{2}$	$\frac{1}{840}$	$\frac{1}{9240}$	$-\frac{1}{924}$
101			9	$\frac{1}{2}$	$\frac{1}{38}$	$\frac{1}{380}$	$-\frac{9}{380}$
102				$\frac{3}{2}$	$-\frac{1}{76}$	$-\frac{1}{760}$	$\frac{9}{760}$

The value of σ_A^{CD} is calculated from (14), where the product $\gamma_A\rho_{10}$ can be readily obtained from Table I for the Auger process (1a) with $S=\frac{1}{2}$ and 1. Equations (20) and Table I show that the strength of a CDAES signal even in this case is of the same order of magnitude as that of the total Auger intensity for most of the transitions considered in this table. Hence CD should readily be measurable also in the angular distribution of spin-resolved Auger electrons.

V. CONCLUSION

Absorption of a CP photon in a gaseous linear molecule is known to create rotational orientation and alignment of the photoexcited target. Out of these two effects, only the orientation depends upon the helicity of the absorbed photon. Therefore its creation is nothing but a manifestation of the circular dichroism even in $E1$ approximation in achiral molecules which are neither polarized nor fixed in space.

The two possible methods suggested hitherto for detecting this orientation and alignment of the target are measurements (i) of degree of polarization of either spontaneous or laser induced fluorescence and (ii) of CDAD of photoelectrons. Both of these techniques have proved to be very successful in studying rotational orientation and alignment of linear molecules. These are nevertheless based on an inherently anisotropic process which involves interaction, in the form of a vector transition operator in the $E1$ approximation, of radiation with a target which already has a nonisotropic distribution of the population of its magnetic sublevels. Furthermore, both orientation as well as alignment will simultaneously influence fluorescence polarization and CDAD. It will therefore probably not be possible to study with either of these processes only the circular dichroic effects manifested even by achiral, unpolarized, rotating linear molecules in the $E1$ approximation.

In this paper we have proposed, on the other hand, an alterative method which will probe only the rotational orientation created in a linear molecule by the absorption of a CP photon. We have called it CDAES and it will be present in both the integrated as well as differential Auger currents. The transition operator which emits an electron in the decay of a rotationally oriented vacancy created by the absorption of a CP photon in the present case is the scalar, interelectronic, Coulomb interaction. For the CDAD to exist, it is, unfortunately, necessary that the Auger electrons be observed along with their spin. But we have shown that for this purpose neither the SOI nor SRI need be included.

We have therefore derived a general expression for the angular distribution of spin-resolved Auger electrons emitted following absorption in a rotating linear molecule in the absence of either of these two interactions. This expression involves, in addition to the total intensity of the Auger transition being considered, rotational orientation and alignment factors plus three parameters $(\beta_A,\gamma_A,\delta_A)$. Of these, two (β_A,δ_A) depend upon the Auger dynamics whereas the remaining (γ_A) is independent of it. Unlike in our previous study in paper I where SOI was included, we find in the present case that the Auger electrons will not be spin resolved unless the photoabsorption step creates rotational orientation of the molecule.

Although absorption of a CP photon creates orientation as well as alignment, we show that the CDAES totally eliminates the effects of the latter and is exclusively determined by the former. The CD in the angular distribution of spin-resolved Auger electrons is shown to be completely characterized by two quantities, namely, σ_A^{CD} the CD in the spin-resolved integrated Auger current, and the ratio δ_A/γ_A. We have suggested simple experiments to determine both of these quantities. Because γ_A is independent of all dynamics, once δ_A/γ_A is known, δ_A can be extracted. σ_A^{CD} involves, on the other hand, the total Auger intensity σ_A, rotational orientation factor ρ_{10}, and the parameter γ_A. Consequently, a knowledge of σ_A^{CD} and of σ_A will determine ρ_{10}. However, for Auger emission taking place via process (1a) when absorption of a photon merely excites, but does not ionize, the molecule, ρ_{10} is also analytically determined. Therefore measurement of the total Auger intensity σ_A is sufficient to know σ_A^{CD} and other related observables in such experiments. Our example shows that CDAES effects are of the same order of magnitude as σ_A. The degree of spin polarization of the total Auger current does not involve even σ_A and the expression obtained herein gives its value completely analytically for process (1a). We have also suggested experiments to determine the parameters β_A and ρ_{20} as well.

Thus CDAES can be used to probe rotational orientation produced in a gaseous linear molecule by the absorption of CP light. Hence circular dichroic effects can be studied in achiral molecules which are neither polarized nor spatially fixed. This procedure can be used to calibrate degree of CP of electromagnetic radiations over a large photon energy range.

Several workers have previously investigated autoionization of photoexcited diatomics. In particular, Lefebvre-Brion and co-workers [17,18] and Bowering *et al.* [19] have studied angular distribution of spin-resolved electrons ejected following photoabsorption in hydrogen halides (e.g., HI and HBr). Although such radiationless decay of a photoexcited molecule corresponds to our process (1a), the actual physical mechanism which ejects an electron in the present case is, nevertheless, very different in many respects from that considered in the Refs. [17–19].

In the previous studies [17–19], for example, it is the SOI which causes autoionization of a molecule following photo-absorption and also spin polarization of the ejected electron. Therefore, in the papers published by Lefebvre-Brion and co-workers [17,18] and by Bowering *et al.* [19], the spin-orbit Hamiltonian of the molecule had been taken into account. These [17–19] autoionizations are in the energy region of the spin-orbit splitting in HI and HBr molecules.

But in the present article, we have totally neglected the effects of both SOI and SRI. The autoionization of the photoexcited molecule in (1a) [and also that of the ion in (1c)] in our case takes place, instead, due to the interelectronic Coulomb interaction. Furthermore, the ejected electron is now spin polarized as a result of the nonstatistical distribution of magnetic substates (i.e., orientation and alignment) produced by the absorption of a photon in the molecule. In addition, unlike Lefebvre-Brion and co-workers [17,18] and Bowering *et al.* [19] we have included the effects of nuclear rotation and also considered CD in our investigations.

Consequently, Refs. [17–19] and this paper investigate physical phenomena which are not only very different but also take place due to different mechanisms. Any direct comparison between two such studies is not feasible.

The experiments on CDAES suggested herein can, on the other hand, be readily performed by little changes in the various apparatuses currently being used by different groups. The essential component of the new experiments, in addition to a Mott detector to measure spin polarization of the observed electron, will be a high-resolution electron spectrometer which can resolve Auger electrons arriving from the production of a (singly or doubly charged) positive molecular ion in different rotational states. Fortunately, several groups have recently developed such a spectrometer in connection with their high-resolution PES studies [20–24]. These developments have made it possible to resolve photoelectrons ejected in the ionization of H_2, N_2, O_2, NO, HI, etc. to various quantum states of their rotational motion.

The apparatus used by Svensson *et al.* [25] in their very recent study of Auger spectroscopy of N_2 can readily be employed by making two above-suggested changes to perform CDAES experiments proposed in this paper. Likewise, the pump-probe-type experiments carried out by Appling *et al.* [26] to investigate CDAD in aligned NO and other diatomic molecules can also be adapted to investigate CDAES merely by adding a Mott detector. The high-resolution electron spectrometer, which monitors photoelectrons in CDAD experiments [26], can now be used to observe Auger electrons emitted in process (1a). These modifications will be applicable also to processes (1b) and (1c) wherein photoelectrons remain unobserved. Similarly, one can carry out the CDAES investigations with minimal changes, on apparatuses like those used by Heinzmann and co-workers [18,19] in their angle and spin-resolved photoelectron spectroscopic studies of hydrogen halides.

The applications discussed in Sec. IV and in Appendixes A and B in this paper are valid for any linear molecule represented by Hund's coupling scheme (b). Therefore CDAES measurements for process (1a) in a diatomic molecule can be compared with the theoretical results given in Appendix B and Table I herein.

ACKNOWLEDGMENTS

This work was supported by the Department of Science & Technology, India, under SP/S2/K-41/90. One of us (S.S.) is thankful to the Council of Scientific and Industrial Research, India, for financial support.

APPENDIX A: ROTATIONAL ORIENTATION AND ALIGNMENT FACTORS FOR A PHOTOEXCITED MOLECULE IN HUND'S COUPLING SCHEMES (a) AND (b)

In the two appendixes to paper I, we have obtained expressions for rotational orientation and alignment parameters for the excited photoion AB^{+*} in process (1b). Those expressions were derived by using the parity-adapted wave functions [11] for both Hund's coupling schemes (a) and (b) and by employing the angular momentum transfer treatment suggested by Greene and Zare [27] for atoms and by Guest, Jackson, and Zare [28] for linear molecules.

In this appendix, on the other hand, we develop rotational orientation and alignment factors for the photoexcited molecule AB^* formed in Eq. (1a). Again, we have employed parity-adapted states and considered both Hund's coupling schemes (a) and (b). But in the present case, absorption of a photon merely excites the molecule without ionizing it. The process (1a) therefore consists, unlike (1b), only of AB^* with no photoelectron. This renders the angular momentum transfer method [27,28] to be inapplicable to the following analysis.

The density matrix $\rho_{\mathrm{ph}}(JMM';1m_\gamma)$ which describes the photoexcited molecule AB^* in (2) when the Auger emission takes place via process (1a) is given by

$$\rho_{\mathrm{ph}}(JMM';1m_\gamma)=(2J_0+1)^{-1}\times\sum_{M_0}\langle JMp|F_{\mathrm{ph}}|J_0M_0p_0;1m_\gamma\rangle\times\langle JM'p|F_{\mathrm{ph}}|J_0M_0p_0;1m_\gamma\rangle^* . \tag{A1}$$

Here $F_{\rm ph}$ is the photoabsorption operator defined by Eqs. (7) and (8) in Ref. [29] in the $E1$ length and velocity approximations, respectively. The photon-frame states $|1m_\gamma\rangle$ for the absorbed photon are given by the expansion (I.A3) in terms of the molecule-frame states $|1\lambda_\gamma\rangle$.

Let us evaluate the density matrix (A1) first in Hund's coupling scheme (a). The molecules AB and AB^* in this case are described, respectively, by the states (I.A2) and (I.4). On using these two expressions along with (I.A3) and performing integration over the product of three rotational harmonics of $\mathcal{D}^J\mathcal{D}^1\mathcal{D}^{J_0}$, we find that the photoabsorption matrix element

$$\langle JMp|F_{\rm ph}|J_0M_0p_0;1m_\gamma\rangle=(-1)^{\Omega-M}\sqrt{(2J_0+1)(2J+1)}\begin{pmatrix} J & 1 & J_0 \\ -M & m_\gamma & M_0 \end{pmatrix}\langle n\Lambda\Sigma\Omega|F_{\rm ph}|n_0\Lambda_0\Sigma_0\Omega_0;1\rangle \tag{A2}$$

in scheme (a). Here we have defined

$$\begin{aligned}\langle n\Lambda\Sigma\Omega|F_{\rm ph}|n_0\Lambda_0\Sigma_0\Omega_0;1\rangle={}&\tfrac{1}{2}[1-(-1)^{J_0+J+P_0+P-2\Omega_0}]\\ &\times\sum_{\lambda_\gamma}\left[\begin{pmatrix} J & 1 & J_0 \\ -\Omega & \lambda_\gamma & \Omega_0 \end{pmatrix}\langle n\Lambda\Sigma\Omega|F_{\rm ph}|n_0\Lambda_0\Sigma_0\Omega_0;1\lambda_\gamma\rangle\right.\\ &\left.+(-1)^{p_0}\begin{pmatrix} J & 1 & J_0 \\ -\Omega & \lambda_\gamma & -\Omega_0 \end{pmatrix}\langle n\Lambda\Sigma\Omega|F_{\rm ph}|n_0\ -\Lambda_0-\Sigma_0\ -\Omega_0;1\lambda_\gamma\rangle\right] .\end{aligned} \tag{A3}$$

For this matrix element not to be trivially zero, we must obviously have

$$J_0+J+p_0+p-2\Omega_0=\text{odd} . \tag{A4}$$

This selection rule is naturally very different from that arrived at in (I.A8) for the photoionization step in (1b) and (1c).

On substituting (A2) in (A1) and defining the photoabsorption cross section

$$\begin{aligned}\sigma_{\rm ph}(JM)={}&\sum_M\rho_{\rm ph}(JMM;1m_\gamma)\\ ={}&\tfrac{1}{3}(2J+1)|\langle n\Lambda\Sigma\Omega|F_{\rm ph}|n_0\Lambda_0\Sigma_0\Omega_0;1\rangle|^2 ,\end{aligned} \tag{A5}$$

the density matrix which represents the photoexcited molecule AB^* in Hund's coupling scheme (a) becomes

$$\rho_{\rm ph}(JMM';1m_\gamma)=3\sigma_{\rm ph}(JM)\sum_{M_0}\begin{pmatrix} J & 1 & J_0 \\ -M & m_\gamma & M_0 \end{pmatrix}\begin{pmatrix} J & 1 & J_0 \\ -M' & m_\gamma & M_0 \end{pmatrix} . \tag{A6}$$

In order to calculate $\rho_{\rm ph}$ in the coupling scheme (b), we use the states (I.B1) for AB and (I.14) for AB^*. The corresponding photoabsorption matrix element is given by

$$\begin{aligned}\langle JMp|F_{\rm ph}|J_0M_0p_0;1m_\gamma\rangle={}&(-1)^{\Lambda+M-S_0}\sqrt{(2N_0+1)(2J_0+1)(2N+1)(2J+1)}\begin{pmatrix} 1 & J & J_0 \\ m_\gamma & -M & M_0 \end{pmatrix}\\ &\times\langle n\Lambda(NS)J|F_{\rm ph}|n_0\Lambda_0(N_0S_0)J_0;1\rangle ,\end{aligned} \tag{A2$'$}$$

with

$$\begin{aligned}\langle n\Lambda(NS)J|F_{\rm ph}|n_0\Lambda_0(N_0S_0)J_0;1\rangle={}&\tfrac{1}{2}[1-(-1)^{N_0+N+p_0+p}]\begin{Bmatrix} N_0 & S_0 & J_0 \\ J & 1 & N \end{Bmatrix}\\ &\times\delta_{SS_0}\sum_{\lambda_\gamma}\left[\begin{pmatrix} N & 1 & N_0 \\ -\Lambda & \lambda_\gamma & \Lambda_0 \end{pmatrix}\langle n\Lambda|F_{\rm ph}|n_0\Lambda_0;1\lambda_\gamma\rangle\right.\\ &\left.+(-1)^{p_0}\begin{pmatrix} N & 1 & N_0 \\ -\Lambda & \lambda_\gamma & -\Lambda_0 \end{pmatrix}\langle n\Lambda|F_{\rm ph}|n_0\ -\Lambda_0;1\lambda_\gamma\rangle\right] .\end{aligned} \tag{A3$'$}$$

In deriving (A2′) and (A3′), we have used the identity from Ref. [30] which expresses a sum over the product of three 3-j symbols into a product of one 3-j symbol and one 6-j symbol. The selection rule

$$N_0+N+p_0+p=\text{odd} \tag{A4$'$}$$

applicable to (A3′) is again very different from the one given in (I.B3). The density matrix which will express the photoabsorption process in (1a) is now obtained by substituting (A2′) in (A1). One finds that the resulting expression is identical to (A6), but the photoabsorption cross section is now given by

$$\sigma_{\mathrm{ph}}(JM)=\tfrac{1}{3}(2N_0+1)(2N+1)(2J+1)\times|\langle n\Lambda(NS)J|F_{\mathrm{ph}}|n_0\Lambda_0(N_0S_0)J_0;1\rangle|^2 \qquad (\mathrm{A5}')$$

in place of (A5).

The state multipoles

$$\langle[T(J,m_\gamma)]^\dagger_{KQ}\rangle=3(-1)^{m_\gamma+K+J_0+J}\delta_{0Q}\sqrt{2K+1}\times\begin{pmatrix}1 & 1 & K\\ m_\gamma & -m_\gamma & 0\end{pmatrix}\begin{Bmatrix}1 & 1 & K\\ J & J & J_0\end{Bmatrix}\times\sigma_{\mathrm{ph}}(Jm) \qquad (\mathrm{A7})$$

for the photoexcited molecule AB in (1a) are obtained by substituting (A6) in (I.3) and using once again the identity given in Ref. [30]. Consequently, the rotational orientation ($K=1$) and alignment ($K=2$) factors (I.13) become

$$\rho_{KQ}(J;m_\gamma)=3(-1)^{m_\gamma+K+J_0+J}\sqrt{2K+1}\delta_{0Q}\times\begin{pmatrix}1 & 1 & K\\ m_\gamma & -m_\gamma & 0\end{pmatrix}\begin{Bmatrix}1 & 1 & K\\ J & J & J_0\end{Bmatrix}. \qquad (\mathrm{A8})$$

In paper I, we have seen that the density matrix (I.A9), state multipoles (I.A11″), as well as the rotational orientation and alignment parameters (I.A13″) all depend upon the photoionization dynamics involved in step 1 of processes (1b) and (1c). In the present case, on the other hand, whereas both ρ_{ph} and $\langle[T(J;m_\gamma)]^\dagger_{KQ}\rangle$ in (A6) and (A7), respectively, involve the photoabsorption cross section (A5) or (A5′), the orientation and alignment factors ρ_{KQ} in (A8) are totally independent of all dynamics. It is completely determined analytically by a product of one 3-j and one 6-j symbol, in addition to energy-independent constants and phase factors. Moreover, even the expressions for ρ_{ph} and $\langle[T(J;m_\gamma)]^\dagger_{KQ}\rangle$ which involve dynamical terms are herein much simpler compared to their counterparts derived in the two appendixes in I. The analysis given in this appendix is applicable to Auger-emission studies described in paper I as well as in the present article.

APPENDIX B: CALCULATION OF $\gamma_A\rho_{10}(J;m_\gamma)$ FOR AUGER EMISSION VIA PROCESS (1a)

In Eq. (17) we have derived an expression for the product $\gamma_A\rho_{10}(J;m_\gamma)$ needed in the calculation of $\sigma_A(m_\gamma;\hat{\mathbf{u}}_A\mu_A)$, $P(m_\gamma;\mu_A)$, and of $\sigma_A^{\mathrm{CD}}(\hat{\mathbf{u}}_A\mu_A)$ for the Auger-emission process (1a). In this appendix, we further simplify this expression and show that it can be completely determined by the quantum number (N,S,J) needed to specify the photoexcited molecule AB^*. Using the values of the 6-j symbols from Ref. [30], one arrives at the following results.

$S_f=S-\frac{1}{2}$, $J_0=1-J$ for $J\le1$:

$$\gamma_A\rho_{10}(J;m_\gamma)=-m_\gamma\frac{A(N,S,J)}{2(J+1)(2J+1)S}, \qquad (\mathrm{B1})$$

$S_f=S-\frac{1}{2}$, $J_0=J-1$ for $J>1$:

$$\gamma_A\rho_{10}(J;m_\gamma)=-m_\gamma\frac{A(N,S,J)}{4J(2J+1)S}, \qquad (\mathrm{B2})$$

$S_f=S-\frac{1}{2}$, $J_0=J$:

$$\gamma_A\rho_{10}(J;m_\gamma)=-m_\gamma\frac{A(N,S,J)}{4J(J+1)(2J+1)S}, \qquad (\mathrm{B3})$$

$S_f=S-\frac{1}{2}$, $J_0=J+1$:

$$\gamma_A\rho_{10}(J;m_\gamma)=m_\gamma\frac{A(N,S,J)}{4(J+1)(2J+1)S}, \qquad (\mathrm{B4})$$

$S_f=S+\frac{1}{2}$, $J_0=1-J$ for $J\le1$:

$$\gamma_A\rho_{10}(J;m_\gamma)=m_\gamma\frac{A(N,S,J)}{2(J+1)(2J+1)(S+1)}, \qquad (\mathrm{B5})$$

$S_f=S+\frac{1}{2}$, $J_0=J-1$ for $J>1$:

$$\gamma_A\rho_{10}(J;m_\gamma)=m_\gamma\frac{A(N,S,J)}{4J(2J+1)(S+1)}, \qquad (\mathrm{B6})$$

$S_f=S+\frac{1}{2}$, $J_0=J$:

$$\gamma_A\rho_{10}(J;m_\gamma)=m_\gamma\frac{A(N,S,J)}{4J(J+1)(2J+1)(S+1)}, \qquad (\mathrm{B7})$$

$S_f=S+\frac{1}{2}$, $J_0=J+1$:

$$\gamma_A\rho_{10}(J;m_\gamma)=-m_\gamma\frac{A(N,S,J)}{4(J+1)(2J+1)(S+1)}, \qquad (\mathrm{B8})$$

where

$$A(N,S,J)\equiv J(J+1)+S(S+1)-N(N+1). \qquad (\mathrm{B9})$$

These expressions will give us $\gamma_A\rho_{10}(J;m_\gamma)$ for all those physically acceptable values of the quantum numbers (N,S,J), and S_f for which this product does not trivially vanish.

From the Pauli exclusion principle, a non-σ (i.e., π, δ, ϕ, etc.) orbital in a linear molecule can contain up to four electrons, whereas only two electrons are allowed in a σ orbital. Therefore the most probable values of the total spin of an electronic state in such molecules are $S=0$, $\frac{1}{2}$, or 1. Expression (17) identically vanishes for $S=0$. In Table I, we have therefore given $\gamma_A\rho_{10}(J;m_\gamma)$ as a function of N for $S=\frac{1}{2}$ and 1 with $J=|N-S|$ to $N+S$, for N varying from 0 to 10. The product $\gamma_A\rho_{10}(J;m_\gamma)$ for values of $S>1$ and $N>10$ can readily be calculated from expressions (B1)–(B9).

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