

Angular anisotropy and dichroism in molecular Auger spectroscopy following photo-absorption

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Abstract. This paper shows that angular distribution of spin-unresolved Auger electrons emitted in the decay of a vacancy created by the absorption of a photon in a certain class of free, unpolarized and gaseous non-linear molecules is completely characterized by three, rather than by two well-known parameters. The presence of this additional third parameter gives rise to circular dichroic effect which varies as cosine of the angle made by the departing Auger electron with the direction of incidence of the circularly polarized radiation. Linear dichroic effect varies as the square of sine of the angle made by the direction of emission of Auger electron and the polar axis of the space frame. Linear and circular dichroism in the angular correlation between the E_i photoelectron and Auger electron emitted sequentially from a molecule belonging to one of the 32 point groups has also been investigated.

Keywords. Circular dichroism; linear dichroism; Auger electron; photoelectron; correlation between photo- and Auger-electron.

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1. Introduction

Angular distribution of spin-unresolved Auger electrons emitted following photoabsorption is given by

$$\frac{d\sigma_a(m_r)}{d\hat{k}_a} = \frac{\sigma_a}{4\pi} \left[1 + \frac{1}{2}(2 - 3m_r^2)\beta_a P_2(\cos\theta_a) \right]. \quad (1)$$

This result was first derived by Flugge *et al* [1] for atomic targets and later shown to be applicable even to linear molecules without [2, 3] or with [4] rotation of their nuclei taken into account. The target in these [1–4] studies is always free and unpolarized in its gaseous state. In eq. (1) σ_a is the integrated Auger current; β_a the Auger asymmetry parameter; m_r specifies the state of polarization of the absorbed photon. Further in (1), $\hat{k}_a(\theta_a, \phi_a)$ is the propagation vector of the Auger electron in the photon (or laboratory)-frame of reference. The polar axis of this frame is taken along the direction of the electric field vector if the absorbed photon is linearly polarized (LP, $m_r = 0$). On the other hand, it is the direction

of incidence which defines the polar axis of our photon-frame for circularly polarized (CP, $m_p = \pm 1$) or unpolarized (UP) beam of radiation. Both σ_a and β_a in (1) depend on the photoabsorption as well as on the Auger decay dynamics.

Flugge *et al* [1] further showed that the asymmetry parameter β_a is different from zero in the non-radiative decay of only those vacancies which are in other than K shell in an atom. But, Dill *et al* [2] found that even K shell vacancies in a linear molecule can be anisotropic giving rise to the angular Auger current (1). The theoretical prediction [2] of an anisotropic K -shell Auger emission has been experimentally observed by Saito and Suzuki [5] and by Yaghisita *et al* [6] in the $N(1s)$ and by Hemmers *et al* [7] in the $C(1s) \sigma^*$ shape resonances of N_2 and CO, respectively. This difference in the behaviour of molecular K shell vacancies from that of their atomic counterparts arises due to the highly anisotropic nature of the photon-molecule interactions [2–7].

In §2 we show that the anisotropy in the molecular interactions gives rise, in principle, to one more term in the angular distribution (1) of Auger electrons emitted following photoabsorption. This term varies as $\cos \theta_a$. The occurrence of this additional term provides not only a new experimental parameter for studying Auger dynamics of molecular targets, but also gives rise to circular dichroism (CD) in angular distribution of spin-unresolved Auger electrons emitted from free and unpolarized, gaseous molecules by the scalar, inter-electronic coulomb interaction. We also discuss some of those circumstances when this term does not vanish identically and show that the condition in which dichroic effect produced by it exists are totally different from those found to be necessary for the existence of CD in the angular distribution of Auger electrons emitted following photoabsorption in rotating linear molecules [8] and in atoms [9].

In §3, we further show that linear and circular dichroism is present also in the angular correlation between photo- and Auger-electrons from a free, unpolarized gaseous molecule belonging to one of the 32 point groups. Therein, we prove that this CD in one photon, two-step, double ionization (i.e., CDDI) of non-linear molecules is $\alpha_{ap} \cos \theta$ for a collinear experimental geometry in which Auger and photoelectrons depart in a line. Here θ is the angle between the polar axis of the photon-frame and the line joining two correlated outgoing electrons. CDDI has already been studied in atoms [10–12] and in rotating linear molecules [13]. Section 4 contains an application of the analysis presented in this paper to molecules whose point symmetry group is T_d , (e.g., CCl_4 , $SiCl_4$, etc) and C_{3v} (e.g., CH_3I , CH_3Cl , etc). The conclusions of this work are described in §5.

2. Auger electron angular distribution and dichroism

In order to formulate a general theory for dichroism for molecular Auger emission processes we need to introduce two concentric frames of reference. These are photon-fixed frame of reference and space (or laboratory)-fixed frame of reference. Polar axis of the photon frame is the direction of incidence (electric vector) for circularly polarized (linearly polarized) light. Let $\omega_p = (\phi_p, \theta_p, \gamma_p)$ be the set of Euler angles which rotates the space frame in photon frame. Following Edmond [14] the rotation matrixes $\mathcal{D}(\omega_p)$ are defined such that

$$Y_L^{N_L}(\hat{k}_a) = \sum_{N'_L} \mathcal{D}_{-N'_L - N_L}^L(\omega_p) Y_L^{N'_L}(\hat{k}'_a),$$

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where unprimed (primed) variable refer to the photon (molecule) frame of reference. $\hat{k}_a(\hat{k}'_a)$ is the direction of propagation of Auger electrons with respect to photon (space) frame.

In eq. (I.22) [15] we have already derived an expression for angular correlation between photoelectrons and Auger electrons emitted from a molecule belonging to one of the 32 point groups. On integrating (I.22) over the direction of propagation $\hat{k}_p(\theta_p, \phi_p)$ of the photoelectron, we obtain angular distribution $d\sigma_a(m_r)/d\hat{k}_a$ of Auger electrons emitted in the decay of vacancy created by the absorption, in electric dipole approximation (*E1*), of a photon in a free, gaseous molecule. This expression can be written as

$$\frac{d\sigma_a(m_r)}{d\hat{k}_a} = \frac{\sigma_a}{4\pi} \left[1 - 2m_r\alpha_a \cos\theta_a + \frac{1}{2}(2 - 3m_r^2)\beta_a P_2(\cos\theta_a) \right], \quad (2)$$

where

$$\sigma_a = \frac{2\pi}{W^*\hbar} S^* \sum_{lm} (2l+1)^{-1} \left| M_{lm}^{(a)} \right|^2 \quad (3a)$$

is the spin-unresolved, integrated Auger current, and

$$\alpha_a = \frac{\pi K_p}{W^*\hbar\sigma_a\bar{\sigma}_p} \sqrt{\frac{3}{2}} S^* \sum_{\substack{l' p_1 \tau_1 \\ Kq h_1 l_1}} (-1)^K (2K+1) \begin{pmatrix} l & l' & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & 1 \\ l & l' & K \end{Bmatrix} \\ M_l(p_1 \tau_1 h_1 l_1; Kq) M_p^*(p_1 \tau_1 h_1 l_1; Kq), \quad (3b)$$

$$\beta_a = \frac{2\pi K_p}{W^*\hbar\sigma_a\bar{\sigma}_p} \sqrt{\frac{10}{3}} S^* \sum_{\substack{l' p_1 \tau_1 \\ Kq h_1 l_1}} (-1)^K (2K+1) \begin{pmatrix} l & l' & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ l & l' & K \end{Bmatrix} \\ M_l(p_1 \tau_1 h_1 l_1; Kq) M_p^*(p_1 \tau_1 h_1 l_1; Kq). \quad (3c)$$

The dynamical terms

$$M_l(p_1 \tau_1 h_1 l_1; Kq) = \sum_{m\lambda_r} (-1)^m \begin{pmatrix} l & 1 & K \\ -m & \lambda_r & q \end{pmatrix} M_{lm}^{(a)} d_{h_1 l_1}^{p_1 \tau_1}(\lambda_r) \quad (4a)$$

present in (3b, c) are the sums of the products of the Auger decay amplitude $M_{lm}^{(a)}$ defined in (I.21a) and of the *E1* photoabsorption matrix elements $d_{h_1 l_1}^{p_1 \tau_1}(\lambda_r)$ given in eq. (10) in [16]. Further in (4a), the photoabsorption cross-section $\bar{\sigma}_p$ and the constant K_p are those given in eq. (12) in [16] and [17], respectively. The symbols not explained herein have meanings identical to those given in paper I.

Thus, complete characterization of the angular distribution of spin-unresolved Auger electrons emitted following photoabsorption in electric dipole (*E1*) approximation in a free and unpolarized gaseous molecule requires three parameters ($\sigma_a, \alpha_a, \beta_a$), instead of the two (σ_a, β_a) considered hitherto [1-7] in eq. (1). But this new term, which is present on the right hand side of eq. (2) and is proportional to $\cos\theta_a$, makes no contribution to

the angular Auger current in any of the following five circumstances : (i) Auger electrons are observed in the X - Y plane of the photon-frame (i.e., $\theta_a = \pi/2$). (ii) The incident beam of radiation is LP (i.e., $m_r = 0$). (iii) The absorbed photon is UP. [In order to obtain angular distribution of Auger-electrons in this case, expression (2) should be averaged over $m_j = \pm 1$.] (iv) The 3- j symbol present in (3b) is zero if $l + l'$ is not odd. This means, for α_a in (2) not to vanish identically, the single-centre expansion of the continuum orbital of Auger electron should contain both even as well as odd partial waves. That is, the molecular target must not have a plane of reflection perpendicular to the molecular axis or a centre of inversion. (v) Let us assume that the nuclear field has cylindrical symmetry, like in linear molecules belonging to the $C_{\infty v}$ or $D_{\infty h}$ point groups. The dynamical term (4a) for such a system becomes

$$M_l(l_1 m_1; Kq) = \sum_{m \lambda_r} (-1)^m \begin{pmatrix} l & 1 & K \\ -m & \lambda_r & q \end{pmatrix} M_{lm}^{(a)} d_{l_1 m_1}(\lambda_r). \quad (4b)$$

Here, $M_{lm}^{(a)}$ is the Auger decay amplitude (I.28a), and the photoionization matrix element $d_{l_1 m_1}(\lambda_r)$ are defined elsewhere [3,14,18]. Because, nuclear field in a linear molecule is cylindrically symmetric, therefore these two amplitude possess the properties (I.29a) and $d_{l_1 -m_1}(-\lambda_r) = d_{l_1 m_1}(\lambda_r)$, respectively. In order to specialize the eqs (2)-(4) to $C_{\infty v}$ and $D_{\infty h}$ targets, one needs to make therein only the following replacement

$$\sum_{\substack{q_1 p_1 \\ \tau_1 h_1}} M_l(p_1 \tau_1 h_1 l_1; Kq) M_{l'}^*(p_1 \tau_1 h_1 l_1; Kq) = \sum_{q=-K}^K \sum_{m_1=-l_1}^{l_1} M_l(l_1 m_1; Kq) M_{l'}^*(l_1 m_1; Kq).$$

This can readily be shown to be zero unless $l + l'$ is even. This, in view of the 3- j symbol present in (3b), immediately means that $\alpha_a = 0$ and $\beta_a \neq 0$ for molecular systems with cylindrical symmetry.

Thus, a free, unpolarized, gaseous non-linear molecule without a centre of inversion and a plane of reflection perpendicular to its axis may, in general, give rise to $\alpha_a \neq 0$ and $\beta_a \neq 0$. Then expression (2), rather than (1), describes the Auger electron angular distribution.

An immediate and important consequence of this general result is the presence of CD

$$\frac{d\sigma_a^{CD}}{d\hat{k}_a} \equiv \frac{d\sigma_a(m_r = +1)}{d\hat{k}_a} - \frac{d\sigma_a(m_r = -1)}{d\hat{k}_a} = \alpha'_a \cos \theta_a \quad (5a)$$

where

$$\alpha'_a = -\sigma_a \alpha_a / \pi, \quad (5b)$$

in the angular distribution of spin-unresolved Auger electrons emitted in the decay of a vacancy created by photoabsorption in $E1$ approximation in a free and unpolarized gaseous molecule. According to the discussion, already presented in this paper, a certain class of non-linear molecules will exhibit this CD in their Auger electron spectroscopy (i.e.,

CDAES). But, in atoms as well as in linear molecules the previously mentioned circumstances (iv) and/or (v) exist. Therefore, for both of these targets, one always has $\alpha_a = 0$. The occurrence of this situation not only gives rise to the distribution (1) or Auger electrons emitted from such systems, but also makes it necessary [8, 9] that their spins too be analysed if one is interested in studying CDAES in atoms and in linear molecules.

Now we calculate from (I.22) linear dichroism (LD)

$$\frac{d\sigma_a^{\text{LD}}}{d\hat{k}'_a} \equiv \frac{d^2\sigma_a(m_r = 0; \hat{p}(\pi/2, \pi/2))}{d\hat{k}'_a d\hat{p}} - \frac{d^2\sigma_a(m_r; \hat{p}(\pi/2, 0))}{d\hat{k}'_a d\hat{p}} = \beta'_a \sin^2 \theta_a \cos 2\phi_a \quad (6a)$$

where

$$\beta'_a = -\frac{1}{4\pi} \sqrt{\frac{15}{2}} \beta_a \sigma_a. \quad (6b)$$

So, from previous discussions we can say LDAES exists for both linear as well as non-linear molecules. $\hat{p}(\equiv \theta_p, \phi_p)$ is direction of the polar axis of photon frame with respect to space frame.

The three parameters present in (2) are readily determined by performing three measurements in succession:

- (a) For σ_a , one measure $(d\sigma_a(m_r))/(d\hat{k}'_a)$ at magic angle ($\theta_a = 54.7^\circ$) following absorption of LP or UP radiation.
- (b) Measurement of linear dichroism (in (6)) and $(d\sigma_a(m_r))/(d\hat{k}'_a)$ in the X - Y plane of the photon-frame for absorbed radiation of any polarization will contain both σ_a and β_a .
- (c) The remaining parameter α_a can readily be extracted by measuring either CD defined in (5) or $(d\sigma_a(m_r))/(d\hat{k}'_a)$ for RCP or LCP photon at the magic angle. While the former measurement will directly give α_a , the latter will contain σ_a and α_a .

3. Dichroism in angular correlation between Auger and photoelectrons

Equation (I.22) for angular correlation between the Auger and photoelectrons from a free, gas phase molecule gives us the following expression for CDDI:

$$\begin{aligned} \frac{d^2\sigma^{\text{CD}}}{d\hat{k}_a d\hat{k}_p} &= -\frac{K_p}{WW^*h} \sqrt{\frac{3}{2}} \mathbf{SS}^* \\ &\sum_{\substack{u_1 l_t \\ l'_1 l'_t}} \sum_{\substack{LL_1 N_L \\ Kq}} (-1)^{l_1+l_t+L+K} (2K+1) \sqrt{(2L+1)(2L_1+1)} \\ &\begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l'_1 & L_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & L_1 & 1 \\ N_L & -N_L & 0 \end{pmatrix} \begin{Bmatrix} l & l' & L \\ l'_t & l_t & K \end{Bmatrix} \begin{Bmatrix} l_1 & l'_1 & L_1 \\ l_t & l'_t & L \\ 1 & 1 & 1 \end{Bmatrix} \\ &M_l(l_1 l_t; Kq) M_{l'_t}^*(l'_1 l'_t; Kq) Y_L^{N_L}(\hat{k}_a) Y_{L_1}^{-N_L}(\hat{k}_a). \end{aligned} \quad (7)$$

Here, the dynamical amplitude

$$M_l(l_1 l_t; Kq) = \sum_{mm_t} \begin{pmatrix} l & l_t & K \\ m & m_t & q \end{pmatrix} M_{lm}^{(a)} d_{l_1}(l_t, m_t) \quad (8)$$

is the linear combination of the products of the Auger decay amplitudes $M_{lm}^{(a)}$ and of the $E1$ photoionization 'reduced' matrix elements $d_{l_1}(l_t, m_t)$ obtained from the respective eqs (I.21a) and (I.21b). The simplified form (7) of the CDDI is obtained by analytically performing the sum over M_L present in (I.22), with the help of the identity (4.16) [19].

Expression (7) shows that CD exists in the $E1$ photoelectrons emitted also from free gaseous molecular targets provided they (photoelectrons) are observed alongwith Auger electrons. This result is applicable to any experimental geometry. It, nevertheless, becomes particularly simple for the following three photon-propagation and electron-detection configurations: (a) when photoelectron is observed along the polar axis out of photon frame, i.e., $\hat{k}_p(\theta_p = 0, \phi_p)$; (b) on detecting Auger electron along the polar axis, i.e., $\hat{k}_a(\theta_a = 0, \phi_a)$; (c) photo- and Auger-electrons depart in opposite directions, i.e., if $\hat{k}_a(\theta_a = 0, \phi_a)$; then $\hat{k}_p(\theta_p = \pi - \theta, \phi_p = \pi + \phi)$. Each of the three cases (a)–(c) will give us CDDI in a coplanar experimental arrangement wherein the detection directions of the Auger and photoelectrons lie in a plane which contains also the polar axis of the photon-frame. While CDDI in both (a) and (b) is expressible in a series of Legendre polynomials of order up to $2l_{\max}$ and $2l_{1\max}$ respectively ($2l_{\max}$ and $2l_{1\max}$ are the highest angular momenta used to represent the continuum molecular orbitals of the Auger and photoelectrons respectively), (c) gives

$$\frac{d\sigma^{\text{CD}}}{d\theta} = \alpha_{ap} \cos \theta, \quad (9a)$$

where

$$\alpha_{ap} = -\frac{K_p}{4\pi W W^* \hbar} \sqrt{\frac{3}{2}} \text{SS}^* \sum_{l_1 l_t} \sum_{L L_1} (-1)^{l_1+l_t+L+K} (2K+1)(2L+1)(2L_1+1) \\ \sum_{l' l'_t} \sum_{K q} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l'_1 & L_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & L_1 & 1 \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} l & l' & L \\ l'_t & l_t & K \end{matrix} \right\} \left\{ \begin{matrix} l_1 & l'_1 & L_1 \\ l'_t & l_t & L \\ 1 & 1 & 1 \end{matrix} \right\} \\ M_l(l_1 l_t; Kq) M_p^*(l'_1 l'_t; Kq). \quad (9b)$$

Therefore, similar to CDAES (5), the CDDI (7) in a collinear experimental arrangement is completely described by a single parameter given in (9). Here θ is the angle which the line joining the Auger and photoelectrons makes with the polar axis of the photon-frame. It obviously vanishes for $\theta = \pi/2$, i.e., if these two electrons are moving out in opposite directions perpendicular to the polar axis. This collinear behaviour of CDDI is both simple as well as interesting.

Let us now consider CD in angular correlation between the Auger and photoelectrons from linear molecules. Using properties (I.29a) and (I.29b) applicable respectively to the Auger decay and the 'reduced' matrix elements due to cylindrical nature of nuclear field

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in $C_{\infty\nu}$ and $D_{\infty h}$ molecules, the dynamical amplitude (8) present in the CDDI (7) can be shown to satisfy the relation

$$M_l(l_1 l_t; K - q) = (-1)^{l_1 + l_t + L + K} M_l(l_1 l_t; K q).$$

With the help of this equation and that of the first two 3- j symbols present in (7), we find that

$$\sum_{q=-K}^K M_l(l_1 l_t; K - q) M_l^*(l_1 l_t; K q) = 0, \quad (10a)$$

unless $(L + L_t)$ is even.

But, one further finds that for an experimental configuration wherein the two electron detectors and the polar axis of laboratory frame (which is along the direction of incidence of the CP radiation) lie in a single plane, i.e., with $n = 0, 1, 2$,

$$\sum_{N_L} \begin{pmatrix} L & L_1 & 1 \\ N_L & -N_L & 0 \end{pmatrix} Y_L^{N_L}(\hat{k}_a) Y_{L_1}^{-N_L}(\hat{k}_a) = 0, \quad (10b)$$

unless $(L + L_1)$ is odd.

In view of the two mutually exclusive condition (10a, b), the CDDI (7) does not exist for linear molecules in a coplanar photon-propagation and electron-detection arrangement. This conclusion is applicable also to the geometries (a)–(c) mentioned in this section, as each of these describes CDDI in a plane which contains also the beam of CP ionizing radiation.

From (I.22) we can derive the expression for LD for the angular correlation between Auger and photoelectrons frame from a free, gas phase molecule, which can be written in the following form

$$\begin{aligned} \frac{d^2 \sigma^{\text{LD}}}{d\hat{k}'_a d\hat{k}'_p} &= \frac{2K_p}{WW^* \hbar} \sqrt{\frac{3}{2}} \text{SS}^* \\ &\sum_{\substack{l_1 l_t \\ l' l'_t}} \sum_{\substack{L L_1 N_L \\ K q}} (-1)^{l_1 + l_t - L_1 + K} (2K + 1) ((2L + 1)(2L_1 + 1))^{1/2} \\ &\begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l'_1 & L_1 \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} l & l' & L \\ l'_t & l_t & K \end{matrix} \right\} \left\{ \begin{matrix} l_1 & l'_1 & L_1 \\ l'_t & l_t & L \\ 1 & 1 & 2 \end{matrix} \right\} \\ &[\mathcal{Y}_{22}^{LL_1}(\hat{k}'_a, \hat{k}'_p) + \mathcal{Y}_{2-2}^{LL_1}(\hat{k}'_a, \hat{k}'_p)] M_l(l_1 l_t; K q) M_l^*(l'_1 l'_t; K q). \quad (11) \end{aligned}$$

Here \mathcal{Y} 's are the bipolar harmonics. Simplifying (11), we have seen LDDI does not vanish for linear molecules in a coplanar geometry.

4. Application

We present in this section an example for experiments on CDAES, LDAES, CDDI, and LDDI. Let us take a non-linear, free, gas phase molecule. If its point symmetry group

is T_d , then it is one of CH_4 , CCl_4 , SiCl_4 , GeCl_4 , CF_4 , etc., and if the point symmetry group is C_{3v} , then it is one of CH_3Cl , CH_3Br , CH_3I , etc. Let us consider the case when vacancy is created in the \underline{ma}_1 orbital of these molecules by the $E1$ photoionization procedure described by (I.31a). The photoionization amplitude $d_{h_1 l_1}^{p_1 \tau_1}(\lambda_r)$ and the corresponding 'reduced' matrix elements $d_{l_i}(l_i m_i)$ needed to describe the photoionization step (I.31a) in the respective CDAES expression (5), LDAES expression (6) and CDDI result (7), LDDI result (11) have already been discussed by Chandra at length elsewhere [16–18].

The second quantity needed in the calculation of the dynamical amplitudes (4) and (8) present in the CDAES (5), LDAES (6) and in the CDDI (7), LDDI (11) respectively, is the matrix element $M_{ln}^{(a)}$ defined by (I.21a). This definition contains the amplitude $A_{hl}^{p\tau}$ specified by (I.32) for the Auger decay step (I.31b) of the ion $M^{++}(\underline{ma}_1)$. (An underline under an orbital indicates a vacancy in that orbital.) The calculation of these amplitudes without including either SOI or SRI has already been discussed by us in §4 in ref. [15]. Here too we follow the same procedure which is based on the standard technique described elsewhere [20]. If we assume, for simplicity, that one of the two vacant orbitals in the electronic configuration of M^{++} after the Auger decay is na_1 belonging to the A_1 IR of a T_d group or C_{3v} then the allowed transitions are only those given for T_d molecular by (27) in [3] and for C_{3v} group transition will be $\underline{ma}_1 - \underline{na}_1 \underline{n'a}_1$, $\underline{ma}_1 - \underline{na}_1 \underline{n'a}_2$ and $\underline{ma}_1 - \underline{na}_1 \underline{n'e}$.

Let us first consider $2a_1 - \underline{na}_1 \underline{n'a}_1$ transition of T_d point group molecules. Here we have $p = a_1$ in (3b) with $\tau, h = 1$ and $l = 0, 3, 4$. For this we get

$$\alpha_a = -\frac{\sqrt{5}\pi}{12W^* \hbar \sigma_a} S^* \left(i \exp \left(i \left(\sigma_3^{(a)} - \sigma_4^{(a)} \right) \right) A_{13}^{a_1 1} A_{14}^{a_1 1^*} + \text{C.C.} \right). \quad (12a)$$

However C.C. represents complex conjugate of the expression preceding letters A 's are the amplitudes $A_{hl}^{p\tau}$ defined by (I.32).

Next, we consider CDAES in T_d point group molecules for $\underline{ma}_1 - \underline{na}_1 \underline{n'a}_2$ transition here $p = a_2, \tau, h = 1$ and $l = 6$ then

$$\alpha_a = 0. \quad (12b)$$

Similarly, CDAES in T_d point group molecules for $\underline{ma}_1, -\underline{na}_1 \underline{n'e}$ transition for $p = e, \tau = 1, 2; h = 1, l = 2, 4$ then

$$\alpha_a = 0. \quad (12c)$$

Now, we consider CDAES in T_d point group molecules for $\underline{ma}_1 - \underline{na}_1 \underline{n't}_1$ transition $p = t_1, \tau = 1 - 3; l = 3, 4, h = 1$, for this, we get

$$\alpha_a = \frac{\pi}{16\sqrt{3}W^* \hbar \sigma_a} S^* \left[\left(\frac{5}{\sqrt{6}} + \frac{15}{2\sqrt{2}} - \frac{13}{4} \right) \times i \exp(i(\sigma_3^{(a)} - \sigma_4^{(a)})) (A_{13}^{t_1 1} A_{14}^{t_1 1^*} + A_{13}^{t_1 2} A_{14}^{t_1 2^*}) + \text{C.C.} \right]. \quad (12d)$$

Similarly, the final case for $\underline{ma}_1 - \underline{na}_1 \underline{n't}_2$ transition of T_d point group molecule with $p = t_2; \tau = 1 - 3; h = 1$, and $l = 1, 2$, we get

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$$\alpha_a = -\frac{\pi}{2\sqrt{5}W^*\hbar\sigma_a} \mathbf{S}^* \left[i \exp \left(i \left(\sigma_1^{(a)} - \sigma_2^{(a)} \right) \right) \left(2A_{11}^{t_2^1} A_{12}^{t_2^1*} - 2A_{11}^{t_2^1} A_{12}^{t_2^2*} \right. \right. \\ \left. \left. + (2A_{11}^{t_2^2} A_{12}^{t_2^2*} - 2A_{11}^{t_2^3} A_{12}^{t_2^3*}) + \text{C.C.} \right) \right]. \quad (12e)$$

We thus see that CDAES; following photoabsorption in the ma_1 orbital of free gas phase of CCl_4 , SiCl_4 and GeCl_4 vanishes for $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$ and $\underline{ma_1} - \underline{na_1} \underline{n'e}$ transitions, but has a non-zero value for the remaining three ($\underline{2a_1} - \underline{na_1} \underline{n'a_1}$, $\underline{2a_1} - \underline{na_1} \underline{n't_1}$ and $\underline{2a_1} - \underline{na_1} \underline{n't_2}$) transitions.

Now we present an application of CDAES in C_{3v} point group, on evaluating expression (3b) we find that $\alpha_a = 0$ for all the transitions (namely $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$, $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$ and $\underline{ma_1} - \underline{na_1} \underline{n'e}$) i.e. CDAES, following photoabsorption in $\underline{ma_1}$ orbital of free gas phase CH_3I , CH_3Br , CH_3Cl vanishes for the three transitions.

Now we consider LDAES in $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$ transition of T_d point group molecules. Here we have $p = a_1$ in (3c) with τ , $h = 1$ and $l = 0, 3$. For this we get

$$\beta_a = \frac{0.54}{W^*\hbar\sigma_a} \mathbf{S}^* |A_{13}^{a_1 1}|^2. \quad (13)$$

Similarly, we have seen for T_d point group molecules for the remaining four transitions (i.e. $\underline{ma_1} - \underline{na_1} \underline{na_2}$, $\underline{ma_1} - \underline{na_1} \underline{n'e}$, $\underline{ma_1} - \underline{na_1} \underline{n't_1}$ and $\underline{ma_1} - \underline{na_1} \underline{n't_2}$) β_a is non-zero.

So, we see that LDAES, following photoabsorption in the $\underline{ma_1}$ orbital of a free, gas phase CCl_4 , SiCl_4 and GeCl_4 exists for the five Auger transitions given by (27) of [3].

Next, we consider application of LDAES in C_{3v} point group molecules.

Let us consider $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$ transition, $p = a_1$, $h = 1$, $l = 0, 1$. For this, we get

$$\beta_a = \frac{2\pi\sqrt{5}}{\hbar W^* \sigma_a \sqrt{15}} \left[\frac{6}{5} - \frac{9}{7}\bar{\beta} \right] \mathbf{S}^* |A_{11}^{a_1 1}|^2. \quad (14)$$

Here, $\bar{\beta}$ is angular asymmetry parameter for photoionization.

We also see, $\beta_a \neq 0$ for $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$ and $\underline{ma_1} - \underline{na_1} \underline{n'e}$ transition.

So, LDAES, following photoabsorption in $\underline{ma_1}$ orbital of free, gas phase of CH_3I , CH_3Br , CH_3Cl exists for $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$, $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$ and $\underline{ma_1} - \underline{na_1} \underline{n'e}$ transition.

The CDDI for the example of T_d molecules considered in this section means that we are studying CD in the angular correlation between the $E1$ photoelectrons emitted from the $\underline{ma_1}$ orbital and the Auger electrons ejected subsequently in one of the transitions (27) in [3]. While the continuum orbital of the photoelectron belongs to the T_2 IR, but that of the Auger electrons may transform according to one of the (A_1, A_2, E, T_1, T_2) IRs of the T_d molecular point group.

In (I.33a) and (I.33b) we have already developed expressions for angular correlation between photoelectron ejected from $\underline{ma_1}$ orbital and the Auger electrons coming out in the respective $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$ and $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$ transitions in a T_d molecule for a general experimental geometry. So CDDI for these two cases can readily be obtained. On substituting (I.33a) in the definition of CDDI, we find

$$\frac{d^2\sigma_{\text{CD}}}{d\hat{k}d\hat{k}_p} = -i \frac{\bar{\sigma}_p}{5W^*\hbar} \left[\frac{1}{3} \left(\frac{6}{7} + \bar{\beta} \right) (2 - \bar{\beta}) \right]^{1/2} \mathbf{S}^* \left\{ [\exp(i(\sigma_0^{(a)} - \sigma_3^{(a)}))] A_{10}^{a_1 1} A_{13}^{a_1 1*} \right.$$

$$+ \text{C.C.}] + \frac{4}{11} \sqrt{\frac{7}{3}} [\exp(i(\sigma_3^{(a)} - \sigma_4^{(a)})) A_{13}^{a_1 1} A_{14}^{a_1 1*} + \text{C.C.}] \times \mathcal{Y}_{10}^{33}(\hat{k}_a, \hat{k}_p) \sin \delta \quad (15a)$$

for two electrons ejected in (I.31a) and $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$ transitions. Here, the phase angle δ is defined by (I.34).

We thus, see that for $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$ transition for T_d molecules, CDDI is not necessarily zero if the Auger electrons are observed along with the photoelectrons. For the second case, corresponding to (I.31a) and $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$ emissions, we use (I.33b) and find

$$\frac{d^2 \sigma_{CD}}{d\hat{k}_a d\hat{k}_p} = 0. \quad (15b)$$

That is, both CDAES as well as CDDI are zero for this transition.

We have calculated CDDI also in the remaining three of the five allowed Auger transitions (27) in [3] and found it, unlike (10b), not to be necessarily zero.

The CDDI for the example of C_{3v} molecules considered in the sub-section means we are studying CD in angular correlation between the $E1$ photoelectrons emitted from the $\underline{ma_1}$ orbital and the Auger electrons ejected subsequently in one of these three ($\underline{ma_1} - \underline{na_1} \underline{n'a_1}$, $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$ and $\underline{ma_1} - \underline{na_1} \underline{n'e}$) transitions. While the continuum orbital of the photoelectron belongs to the A_1 and E IR, but that of the Auger electrons may transform according to one of the (A_1, A_2, E) IRs of the C_{3v} molecular point group.

Assuming $A_{hl}^{p\tau} = |A_{hl}^{p\tau}| e^{i\alpha^a}$ and using (7) we find CDDI for $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$ transition of C_{3v} point group ($p = a_1, \tau h = 1, l = 0, 1, 2$ and $m = 0$)

$$\begin{aligned} \frac{d^2 \sigma^{CD}}{d\hat{k}_a d\hat{k}_p} &= \frac{\bar{\sigma}_p \bar{\beta}}{7\pi W^* \hbar} \sqrt{\frac{3}{2}} S^* \left\{ \frac{1}{2\sqrt{15}} \left(\frac{7}{\bar{\beta}} - 1 \right)^{1/2} |A_{10}^{a_1 1}| \sin \theta_a \sin \theta_p \times \right. \\ &\quad \left(11 |A_{10}^{a_1 1}| \sin(\sigma_0^{(a)} - \sigma_1^{(a)} + \alpha_1^{(a)} - \alpha_2^{(a)}) \right. \\ &\quad \left. - \frac{18}{\sqrt{5}} |A_{12}^{a_1 1}| \sin(\sigma_1^{(a)} - \sigma_2^{(a)} + \alpha_1^{(a)} - \alpha_2^{(a)}) \right) \times \\ &\quad \cos(\sigma_0^{(p)} - \sigma_1^{(p)} + \alpha_0^{(p)} - \alpha_1^{(p)}) + 3\sqrt{\frac{5}{2}} \sin \theta_a \sin \theta_p \times \\ &\quad \frac{1}{2} \sin \theta_a \sin \theta_p \cos 2(\phi_a - \phi_p) - \cos \theta_a \cos \theta_p \cos 2(\phi_a - \phi_p) \times \\ &\quad (|A_{10}^{a_1 1}| |A_{12}^{a_1 1}| \cos(\sigma_0^{(a)} - \sigma_2^{(a)} + \alpha_0^{(a)} - \alpha_2^{(a)}) - \frac{1}{5} |A_{11}^{a_1 1}|^2 \\ &\quad + \frac{1}{7} |A_{12}^{a_1 1}|^2 + \frac{1}{120\sqrt{5}} \left[((2 \cos^2 \theta_p - \sin^2 \theta_p) \cos \theta_a \right. \\ &\quad \left. - 3 \sin \theta_a \cos \theta_p \sin \theta_p \cos(\phi_a - \phi_p)) \times \right. \end{aligned}$$

$$\begin{aligned}
 & \left(\frac{|A_{10}^{a_1}|^2}{\sqrt{3}} + \frac{2}{\sqrt{5}} |A_{11}^{a_1}| |A_{12}^{a_1}| \sin(\sigma_1^{(a)} - \sigma_2^{(a)} + \alpha_1^{(a)} - \alpha_2^{(a)}) \right) \\
 & + \frac{3}{175} |A_{11}^{a_1}| |A_{12}^{a_1}| \sin(\sigma_1^{(a)} - \sigma_2^{(a)} + \alpha_1^{(a)} - \alpha_2^{(a)}) \times \\
 & \left(\frac{5}{4} \cos \theta_a \sin^2 \theta'_a \sin^2 \theta_p \cos(\phi_a - \phi_p) - (4 \cos^2 \theta'_a \sin \theta_a \right. \\
 & \left. - \sin^3 \theta_a) \cos \theta_p \sin \theta_p \cos(\phi_a - \phi_p) - (4 \cos^2 \theta_a \sin \theta_a - \sin^3 \theta_a) \right. \\
 & \left. \cos \theta_p \sin \theta_p \cos(\phi_a - \phi_p) - \frac{1}{4} (2 \cos^3 \theta_a - 3 \cos \theta_a \sin^2 \theta_a) \times \right. \\
 & \left. (2 \cos^2 \theta_p - \sin^2 \theta_p) \right) \Bigg] \Bigg\}. \tag{16}
 \end{aligned}$$

So, CDDI is non-zero for $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$ Auger transitions if the Auger electrons are observed along with the photoelectrons.

We have calculated CDDI also in the $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$ and $\underline{ma_1} - \underline{na_1} \underline{n'e}$ Auger transitions and found, like (16) not to be necessarily zero.

We thus see that, although there is no CDAES for the Auger transition $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$, $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$ and $\underline{ma_1} - \underline{na_1} \underline{n'e}$ transitions of C_{3v} molecules, CDDI is not necessarily zero if the Auger electrons are observed along with the photoelectrons.

The LDDI for T_d molecules considered here, means that we are studying LD in the angular correlation between $E1$ photoelectron (whose continuum orbital belongs to T_2 IR) emitted from the ma_1 orbital and Auger electrons (which can belong to one of the (A_1, A_2, E, T_1, T_2 IRs) ejected subsequently in one of the transitions (27) in [3].

Let us consider LDDI in $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$ transition of T_d point group. Here, we have $p = a_1$ in (11) with $\tau, h = 1$ and $l = 0$. We find LDDI is

$$\frac{d^2 \sigma^{LD}}{d\hat{k}'_a d\hat{k}'_p} = -\frac{7\bar{\sigma}_p}{40W^* \hbar} (2.06 + 3.25\bar{\beta}) \sin^2 \theta'_p \cos 2\phi'_p S^* |A_{10}^{a_1}|^2. \tag{17}$$

So, LDDI is non-zero for $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$ Auger transitions.

We have also calculated LDDI in $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$, $\underline{ma_1} - \underline{na_1} \underline{n'e}$, $\underline{ma_1} - \underline{na_1} \underline{n't_1}$ and $\underline{ma_1} - \underline{na_1} \underline{n't_2}$ Auger transitions in T_d molecules and found LDDI has non-zero value for these four transitions.

We also studied LDDI in C_{3v} point group molecules, where the $E1$ photoelectrons emitted from ma_1 orbital and the Auger electrons ejected in one of these three ($\underline{ma_1} - \underline{na_1} \underline{n'a_1}$, $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$, and $\underline{ma_1} - \underline{na_1} \underline{n'e}$) transitions. The continuum orbital of the photoelectrons belong to A_1 and E IR, but that of Auger electrons may belong from one of the (A_1, A_2, E) IRs of C_{3v} molecular point group.

Now, we consider LDDI in $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$ transition or C_{3v} point group molecules. Here we have $p = a_1$ in (11) with $l = 0$. For this we get

$$\frac{d^2 \sigma^{LD}}{d\hat{k}'_a d\hat{k}'_p} = -\frac{301\bar{\sigma}_p}{1260\pi\sqrt{5}W^* \hbar} \bar{\beta} \sin^2 \theta'_p \cos 2\phi'_p S^* |A_{10}^{a_1}|^2. \tag{18}$$

We also see LDDI, like (18), is also non-zero for $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$ and $\underline{ma_1} - \underline{na_1} \underline{n'e}$ Auger transitions of C_{3v} molecules.

5. Conclusion

We have shown that the angular distribution of spin-unresolved Auger electrons emitted in the decay of a vacancy created by the absorption of a CP photon in a certain class of free, unpolarized, gaseous, non-linear molecules is completely described by terms of degree zero, one, and two in $\cos \theta_a$. The presence of the term linear in $\cos \theta_a$ gives rise to the possibility of performing an experiment in which the angular distribution difference for absorption of RCP and LCP radiation is measured. This additional term is shown to be non-zero for $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$, $\underline{ma_1} - \underline{na_1} \underline{n't_1}$ and $\underline{ma_1} - \underline{na_1} \underline{n't_2}$ Auger transitions and zero for $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$ and $\underline{ma_a} - \underline{na_1} \underline{n'e}$ Auger transitions in CCl_4 , $SiCl_4$, and $GeCl_4$ molecules and also zero for $\underline{ma_1} - \underline{na_1} \underline{n'a_1}$, $\underline{ma_1} - \underline{na_1} \underline{n'a_2}$ and $\underline{ma_a} - \underline{na_1} \underline{n'e}$ Auger transitions in CH_3Cl , CH_3Br , CH_3I molecules. The present paper further shows the existence of LDAES; CDDI and LDDI in angular correlation between photo- and Auger-electrons ejected from molecules belonging to one of the 32 point groups. These LDAES, LDDI and CDDI have also been calculated by us for five different transitions in each of CCl_4 , $SiCl_4$, and $GeCl_4$ and three different transitions in each of CH_3Br , CH_3I and CH_3Cl .

Schonhense [21], in connection with circular dichroism in photoelectron angular distribution (CDAD) in molecules fixed in space, had argued that, in order to observe dichroic effects in achiral systems, the experimental geometry must possess chirality, i.e., be characterized by three non-coplanar vectors. (These, in the case of CDAD in fixed molecular systems, are the direction of incidence of CP ionizing radiation, axis of the molecule, and propagation vector of photoelectron.) But, several subsequent investigations [22–26] have revealed that the requirement of a chiral experimental geometry, suggested by Schonhense [21] for the existence of CD in achiral systems, is neither sufficient nor necessary.

Chandra and Sen studied CDAES in spin-resolved, integrated Auger current emitted following absorption of a CP photon in a rotating linear molecule [8] and in an atom [9]. Here, again, two vectors (namely, the directions of incidence of CP radiation and of spin-polarization of Auger electrons) are present in an experiment. Their [8, 9] investigations further revealed that CDAES may be present in the differential Auger current too if the spin-resolved Auger electrons are observed in the same plane which contains the other two vectors as well.

We have shown that spin-unresolved CDAES is specified by only two directions and is proportional to $\cos \theta_a$. Similarly, spin-unresolved CDDI may exist in a coplanar experimental arrangement. Both of these results are, however, applicable to free, non-linear molecules only. We also have shown the existence of LDAES and LDDI exist also for these cases, in free both linear and non-linear molecules.

Measurement of spin-polarization of electrons is an extremely difficult experiment. The main reason for this difficulty is that there is a significant loss (approximately by a factor of 1000 [27]) of intensity in a Mott detector used to observe the direction of quantization of the spin of an Auger electron. Thus this study is experimentally more feasible compared to the investigations performed by Chandra and Sen [8, 9].

The CDAES, LDAES, CDDI and LDDI processes proposed here provide two new experimental parameters for studying Auger dynamics of an electron–electron correlation in

free, unpolarized, gas phase molecules. CDAES and CDDI can also be used to calibrate the degree of CP of the electromagnetic radiation over a wide range of their wavelengths.

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